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DIESEL CRANKCASE EMISSIONS CHARACTERIZATION

by

Charles T. Hare
Daniel A. Montalvo

FINAL REPORT
of
Task No. 4
Contract 68-03-2196

for

Environmental Protection Agency
Emission Control Technology Division
2565 Plymouth Road
Ann Arbor, Michigan 48105

May 1977

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The objective of this project was to characterize crankcase or "blowby" emissions from two in-service diesel engines, developing and demonstrating methodology for analyses where none existed. Methodology development and demonstration was performed using a dynamometer mounted Detroit Diesel 6V-71, and characterization was done on a Cummins NTC-350 and another 6V-71.

Gaseous emissions measured included: emission mass rate; HC, CO, CO_2, and NOx (both exhaust and crankcase emissions); individual hydrocarbons; aldehydes; and N-dimethylnitrosamine. Crankcase particulate measurements included: mass rate; concentration; size distribution; elemental composition; sulfate; total solubles; BaP in solubles; boiling range of solubles; and N-dimethylnitrosamine. These measurements were made using variations of the standard 13-mode diesel procedure.

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Approved:
Karl J. Springer
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Department of Emissions Research
Automotive Research Division

FOREWORD

This report covers Task Order No. 4 of EPA Contract No. 68-03-2196 conducted for the Emissions Control Technology Division, U.S. Environmental Protection Agency, 2565 Plymouth Road, Ann Arbor, Michigan 48105. The EPA Task Officer on this Task Order was Mr. Thomas M. Baines, and the Project Officer was Mr. Merrill W. Korth. Principal investigator for Southwest Research Institute was Charles T. Hare, and he was assisted by Daniel A. Montalvo. Overall supervision was provided by Karl J. Springer. The project was performed during the period February 1976 through April 1977, and it was identified within the Institute as Project No. 11-4291-004.

ABSTRACT

The project described herein was intended to characterize crankcase or "blowby" emissions from two in-service diesel engines, developing and demonstrating methodology for analyses where none existed. These goals were achieved, and a substantial amount of data is now available as a result. Methodology development and demonstration was performed using a dynamometer-mounted Detroit Diesel 6V-71 research engine, and characterization was subsequently done on a truck with a Cummins NTC-350 engine and another 6V-71 which was removed from a city bus and operated on an engine dynamometer.

Crankcase gaseous emissions measured, with prior methodology development where necessary, included: emission mass rate; HC, CO, CO_2, and NO_x (in both exhaust and crankcase emissions); individual hydrocarbons; aldehydes; and N-dimethylnitrosamine. Crankcase particulate measurements included: mass rate; concentration; size distribution; elemental composition including carbon, hydrogen, nitrogen, sulfur, and metals; sulfate; total solubles; BaP in solubles; boiling range of solubles; and N-dimethylnitrosamine. These emissions were measured for either individual modes of the 13-mode diesel procedure or as a composite for the procedure as a whole.

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I. SUMMARY AND CONCLUSIONS

The objectives of this Task Order, which were to develop, demonstrate, and utilize methods for sampling of crankcase emissions from heavy-duty diesel engines, have been achieved. Methods for sampling were developed from scratch where necessary, but were adapted from methods currently in use for exhaust sampling if at all possible. Analytical methods were mostly derived from diesel exhaust analysis experience, although the composition of the crankcase emissions made necessary a number of refinements and modifications. Development of methods was carried out on a dynamometer-mounted Detroit Diesel-Allison 6V-71 test engine (referred to as the "6V-71 development" engine), and characterization was performed on a truck-tractor powered by a Cummins NTC-350 engine and on a 6V-71 bus engine which had been removed from its chassis. The development engine and the NTC-350 were operated on a No. 2 fuel having 0.23 percent sulfur content, and the bus engine was operated on a No. 1 fuel containing 0.10 percent sulfur. The development engine was run on No. 2 fuel because this fuel was necessary for some other research being conducted on the engine at the time. The No. 2 fuel was not necessarily considered "typical" for the 6V-71 development engine.

Exhaust gaseous emissions (regulated pollutants, or HC, CO, and NO_x) were measured along with crankcase emissions, and it was found that crankcase gaseous HC was emitted at the rate of 0.20 to 4.1 percent of exhaust HC. Carbon monoxide and NO_x emitted from the crankcases ranged from 0.005 to 0.43 percent of their counterparts in exhaust gases. Individual low-molecular-weight hydrocarbons (total) were emitted from crankcases at concentrations of 3.5 to 20 ppm C, and aldehydes at concentrations of 9.0 to 15.0 mg/m^3 (2.8 to 4.7 ppm as butyraldehyde). Total crankcase flowrates varied with engine operating conditions, larger flows being emitted as engine speed and load increased. The range of these flows was from 2.4 m^3/hr on the 6V-71 development engine to 10.8 m^3/hr on the turbocharged NTC-350. Crankcase flows were much smaller than engine intake air flows, ranging from about 0.25 to 1.0 percent of air flow when compared on the basis of 13-mode composites.

Analysis for benzo(α)pyrene (BaP) was conducted on crankcase particulate. The analysis included a step in which H_2SO_4 was added to scrapings from the TLC (thin-layer chromatograph) plate to form a fluorescent material for quantitative measurement. Newer techniques do not include this step, and produce lower BaP values which are considered more accurate than those reported here. The BaP values are useful on a comparative basis, however. With this qualification in mind, mass flowrates computed from these crankcase studies ranged from 10 to 77 μg per hour. For comparison, a typical BaP rate in the exhaust particulate of the 6V-71 development engine was 1670 μg per hour (all based on 13-mode composite).

Blowby particulate mass rates measured during this Task Order ranged from about 0.80 to 2.4 g/hr, and the range of concentrations was approximately 93 to 628 mg/m^3. These concentrations were as high as or higher than particulate concentrations found in the exhaust gases of heavy-duty diesels (range approximately 50 to 100 mg/m^3), but crankcase particulate mass emission rates are much lower than those in exhaust due to the smaller crankcase flowrates. Exhaust particulate mass emissions from engines similar to the test engines ranged from approximately 35 to 86 g/hr. The particulate matter from the crankcases was predominantly organic soluble material, ranging from about 88 to 98 percent solubles as determined by Soxhlet extraction. Soluble content of crankcase particulate from the 4-stroke engine was virtually identical to the average of that from the two 2-stroke engines. Comparable figures for exhaust particulate, however, are 50 percent solubles for 2-stroke engines and 10 to 20 percent solubles for 4-stroke engines.

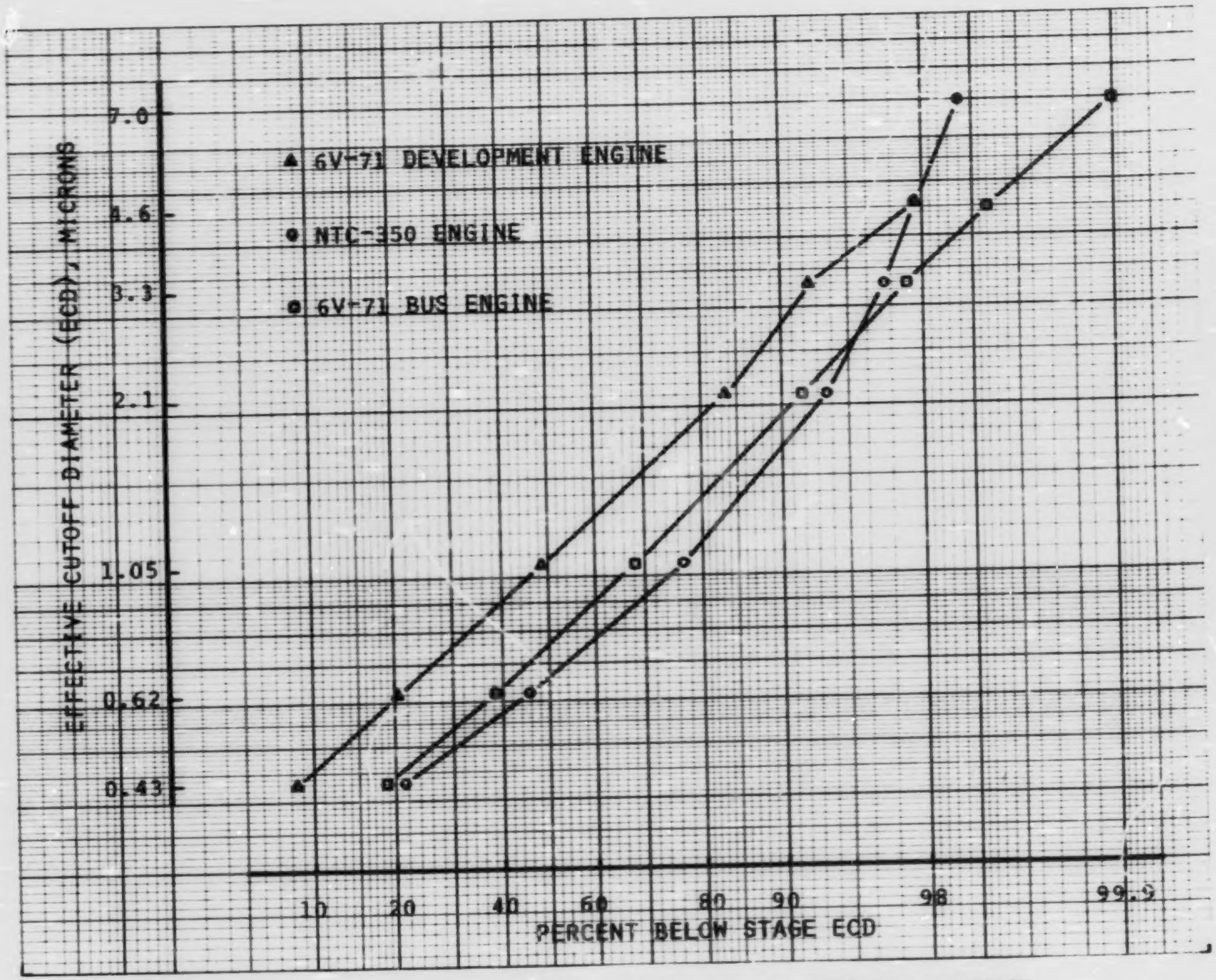
Sulfate emission rates from engine crankcases ran from 0.93 to 2.39 mg/hr in this study, and comparable exhaust emission rates using a fuel with 0.23 percent by weight sulfur content are around 1,300 mg/hr. Exhaust sulfate rates using a low-sulfur fuel (0.04 percent) in a 6V-71 bus engine are around 210 mg/hr at standard engine speeds and 330 mg/hr at low speeds (900 and 1500 rpm). Sulfur in the sulfate emissions from diesel crankcases constituted an average of about 15 percent of the total sulfur in the crankcase particulate.

Particulate from crankcases studied under this Task Order bore a great similarity to lubricating oil according to a number of criteria. Boiling ranges of the soluble fractions of particulate were very similar to those of oils from the respective engines, although slightly wider (that is, solubles contained slightly more low-boiling and high-boiling materials than oils). Carbon and hydrogen content of solubles were only slightly lower than that of oils in general, although two outlying data points tend to confuse the results. Small amounts of ash or other contaminants in particulate could account for carbon/hydrogen differences between oils and particulate. Percentages of sulfur and phosphorus determined by X-ray were similar for oils and solubles, but calcium was found only in the oils. The remainder of the elements showed mixed results.

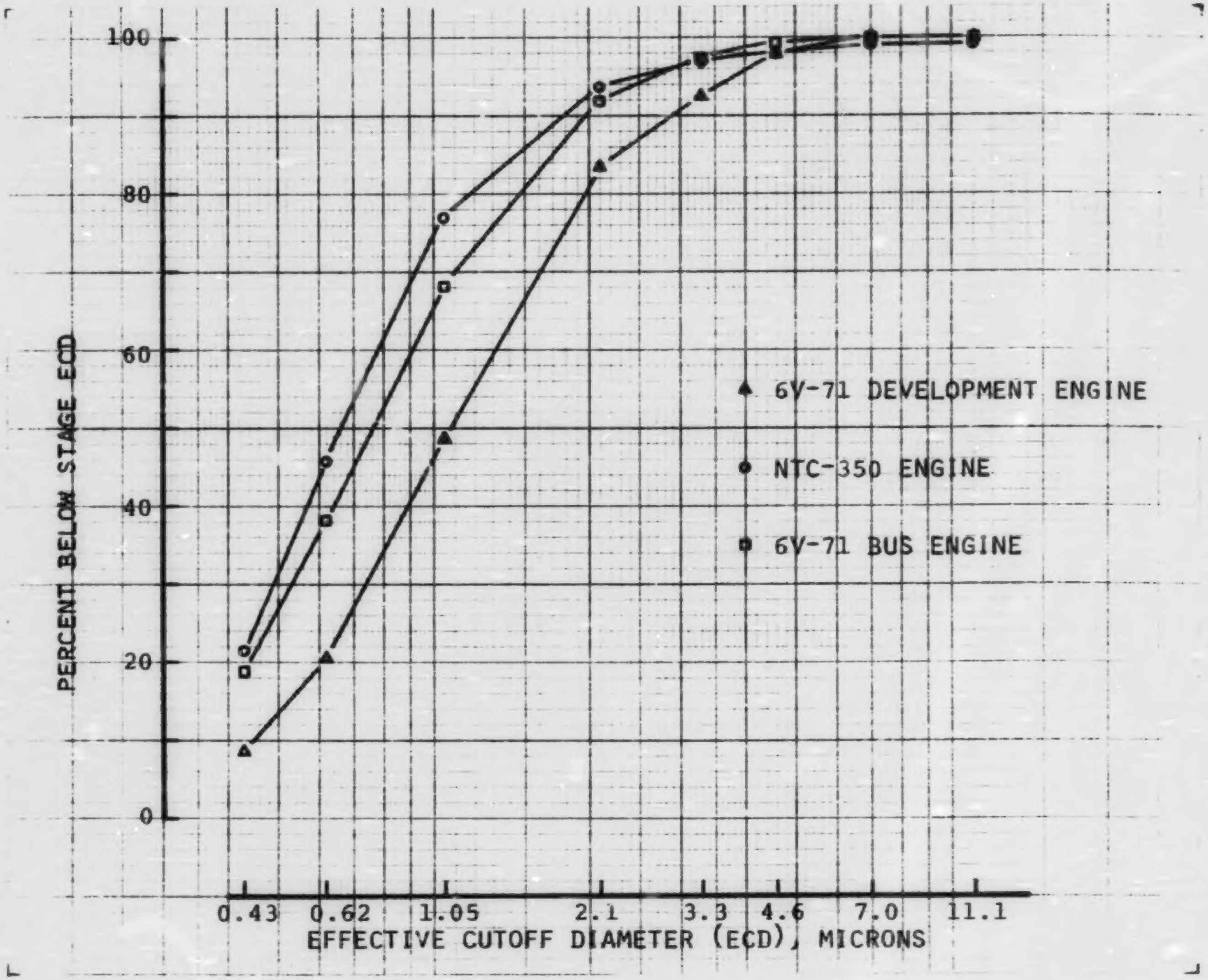
Particulate size distributions from the three engines were somewhat different, but bore a general similarity to one another. Average data from the impactor studies are presented in Summary Figures A and B, a log-probability and a semilog plot, respectively. Crankcase particulate from the 6V-71 development engine was distributed more toward the larger sizes than that from other two engines over most of the size range.

Prior to this research Task, nitrosamines had not been found as an air pollutant emitted by internal combustion engines. No nitrosamines were found in any of the intake air, crankcase particulate, or reagent blank samples analyzed in this Task. Three methods were employed to sample crankcase gases for nitrosamine and nitrosamine precursor analysis, including basic impingers (in two sizes), acidic impingers, and absorptive (Tenax-GC) columns. A fourth engine was also used for some of the nitrosamine sampling. It was a turbocharged 4-stroke Mack ETAY(B)673-A.

No nitrosamine precursors were found in the acidic impinger samples, although the ion chromatographic analysis used was very coarse. No recognized nitrosamine precursors or nitrosamines were found on the Tenax-GC cartridges by GC-MS, although relatively high concentrations of N,N-dimethylacetamide were found. It is uncertain at this writing if there is a possibility that N,N-dimethylacetamide could be a nitrosamine precursor or a compound formed by a reaction of a nitrosamine with some other material.



SUMMARY FIGURE A. LOG-PROBABILITY PLOT OF 13-MODE COMPOSITE CRANKCASE PARTICULATE SIZE DISTRIBUTION FOR THREE TEST ENGINES



SUMMARY FIGURE B. SEMILOG PLOT OF 13-MODE COMPOSITE CRANKCASE PARTICULATE SIZE DISTRIBUTION FOR THREE TEST ENGINES

Indications of nitrosamines were found in basic impinger-collected samples by both SwRI's Department of Environmental Sciences and EPA's National Enforcement Investigations Center. Since no qualification of the sampling methodology was performed, these results cannot be construed as positive identification. GC-MS work performed on a relatively large sample gave strong evidence that one of the compounds measured in the other samples was in fact N-dimethylnitrosamine, but these results do not diminish the possibility that nitrosamines are formed as artifacts in the impinger solution either during or after sampling.

Apparent DMNA concentrations in the crankcase gas samples taken from one development engine and two characterization engines ranged from 27 to 170 ppt (parts per trillion). These concentrations translate to a range of apparent DMNA mass flowrates from 0.35 to 5.5 μg/hr.

A brief examination of available opinion and data on the status and feasibility of crankcase emission controls for diesel engines has been made. Some naturally-aspirated engines are equipped with control systems at the factory, and at least one retrofit kit is offered for stationary and marine engines. Control systems for both naturally-aspirated and turbocharged engines appear to be feasible with existing technology if the necessity for such controls exists.

Based on the above summary and the supporting data found throughout the report, a number of conclusions have been drawn. The most important conclusions are:

1. Although crankcase particulate matter seems very close to lubricating oil in composition (boiling range, elemental analysis), enough differences exist to indicate that such particulate is not simply droplets which have been removed from the oil mechanically. Reasons for this conclusion are the slightly wider boiling range and lack of calcium in particulate.

2. Crankcase gas flows are much smaller than intake air flows, so most gaseous and particulate crankcase emissions are very small as compared to corresponding exhaust emissions. Examples of such pollutants include the following:

Pollutant	% of Corresponding Exhaust Emission
gaseous HC	0.2 - 4.1
CO, NO_x, CO_2	0.005 - 0.43
total particulate	0.9 - 2.9
sulfate ($SO_4^{=}$)	0.07 - 0.7
BaP	0.6 - 4.6
aldehydes	0.2 - 1.0

3. Crankcase particulate matter can be sized with apparent accuracy by an inertial impactor, but deposition on surfaces other than collection discs seems to prohibit use of the device for particle mass flow computations.

4. Analyses conducted for nitrosamines and nitrosamine precursors in crankcase gases were inconclusive. No nitrosamines or precursors were found in crankcase particulate or engine intake air samples. Basic impinger-collected samples appeared to contain DMNA at levels indicative of 27 to 170 ppt (parts per trillion) in crankcase gases, and possibly other nitrosamines at lower levels. Cartridge samples appeared to contain no nitrosamines or known precursors but did contain substantial amounts of N,N-dimethylacetamide. It is concluded that further research should be performed to qualify and employ the most accurate possible nitrosamine methodology for both sampling and analysis of diesel crankcase gases.

5. Systems for control of diesel crankcase emissions are not yet in widespread use. Data should be acquired on performance and durability effects of such systems. Design technology for adequate recirculation or other control systems appears to be available, should it be shown necessary by further characterization studies.

II. TEST PLAN AND METHODOLOGY DEVELOPMENT

The original test plan for this Task Order essentially duplicated the Scope of Work contained in the Task Specification Change Request for Task 4, issued on January 29, 1976. A copy of the aforementioned Scope of Work and subsequent additions are given as Appendix A of this report. The first part of this section contains test plan details, and the second part contains details of sampling and analysis methodology development. Methodology for the sampling and analysis of nitrosamines is covered in Section VI.

A. Development of Test Plan

Criteria used in developing the Test Plan included test runs sufficient to measure or collect samples for all exhaust and blowby constituents of interest, constraints on sample size and acquisition rates imposed by analytical sensitivity and sampling hardware, and enough data points for assessment of repeatability. Many of the sampling and analytical methods used were derived from experience gained under EPA Contract No. 68-02-1230(1)* and (current) Contract No. 68-02-1777. Previous work done on crankcase emissions from diesels(2) was found to be quite rudimentary, which is not surprising since it was published in 1964. It did provide some insight, however, into expected blowby flowrates.

The Test Plan (or sampling and analysis plan) developed for this project is outlined in Table 1, including contaminants sampled, methods, and numbers of determinations. Exhaust gas concentrations were measured during the same modes as crankcase gas concentrations to provide a basis for comparison. The engine operating procedure for all test work was the EPA "13-mode" test(3), or some variation thereof with shorter times in each mode.

It was intended that methodology be developed and demonstrated by performing the analyses shown in Table 1 on a dynamometer-mounted Detroit Diesel-Allison (DDAD) 6V-71 engine in use on another EPA contract (68-02-1777). This plan was followed, and then attempts were made to obtain two other engines (in trucks) for characterization. By agreement with the Project Officer, original criteria used for selection of the characterization engines were:

- one engine should be a 4-stroke, naturally-aspirated engine and the other should be a 2-stroke, non-turbocharged engine

- both engines should have accumulated approximately one half the service normally accumulated before overhaul (125,000 to 200,000 miles, depending on the type of service)

- both engines should have accumulated usage such that they are approximately halfway through the normal oil change interval since an oil change, and they should be tested with the existing oil in the crankcase

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* Superscript numbers in parentheses refer to List of References at end of this report.

- both engines should be mounted in vehicles suitable for chassis dynamometer operation.

In order to complete the test program, some deviations from these criteria were necessary. Although a great deal of effort was expended, no trucks having the required engines were located in the area. The primary difficulties were that 2-stroke engines meeting the service criteria were unavailable, and that all the naturally-aspirated, 4-strokes available had closed crankcases (blowby recirculation). Two-stroke engines were found in buses, and a bus was obtained for testing. This vehicle proved unsuitable for chassis dynamometer operation, however, in that it experienced two tire failures before even one 13-mode sequence could be accomplished.

TABLE 1. TEST PLAN FOR DIESEL CRANKCASE EMISSIONS CHARACTERIZATION

Sample Source	Analysis for	Collection and Analysis Method(s)	Determinations
Crankcase gases	HC, CO, CO_2, NO_x	bag samples, continuous analyzers	3
	aldehydes	DNPH	3
	individual HC	bag samples, G.C.	3
	nitrosamines	wet or column collection, separation or elution, G.C. and GC-MS	5
Crankcase particulate	total particulate	filtration, weighing	30[a]
	sizing	impactor, weighing	5
	appearance and visual sizing	S.E.M. and photography	5[b]
	C, H, N, S	filtration, combustion	5
	elements (metals)	filtration, X-ray	5
	sulfate	filtration, BCA	5
	total organic solubles	filtration, extraction	5
	BaP in solubles	T.L.C.	5
	boiling range of solubles	G.C.	5
	nitrosamines	extraction, G.C.	5
Exhaust gases	HC, CO, CO_2, NO_x	continuous analyzers	3

[a] performed on samples collected for other analyses

[b] S.E.M. work intended as a cross-check on impactor sizing study

The vehicle and the engine finally characterized were a truck-tractor with Cummins NTC-350 (turbocharged 4-stroke) engine and a city bus 6V-71 engine removed from the bus and tested on a stationary dynamometer. Identification and service data on these vehicles/engines is given in Table 2, indicating that they met the total service and oil service criteria quite well.

TABLE 2. IDENTIFICATION AND SERVICE DATA ON CHARACTERIZATION ENGINES

Engine type	Turbocharged 4-stroke	Roots-scavenged 2-stroke
Engine model	Cummins NTC-350	Detroit Diesel-Allison 6V-71
Engine serial number	10370038 (mfd. 9/73)	64A37135
Vehicle source	ABC Truck Rental	San Antonio Transit Company
Vehicle identification	No. 2200, Texas plate R32-988	Original Bus No. 757 - now No. 695
Vehicle model	1974 White Freightliner	GM Truck and Coach - City Coach
Total engine service, km (mi)	337,067 (209,444)	627,762 (390,074)
Service since overhaul, km (mi)	no overhaul	226,059 (140,467)
Normal oil change interval, km (mi)	24,140 (15,000)	8,047 (5,000)
Service since oil change, km (mi)	17,038 (10,587)	4,828 (3,000)

Note: Short overhaul on city bus engine after testing four, stuck rings on two cylinders, some wrist pin wear, no excessive bearing wear

Both engines were tested with the existing oil in the crankcase, and all oil added during the testing periods came from the normal sources (e.g., make-up oil supplies of ABC and San Antonio Transit).

B. Development of Sampling and Analysis Methodology

Re-examining the test plan in Table 1, only the exhaust gas analysis requires no explanation of either sampling or analysis technique.(3) Details of analysis are given in reference only for the following (summaries will be given in text):

DNPH method for aldehydes(4),
G.C. method for individual HC(5), and
BCA method for sulfate.(6)

All other sampling and analysis procedures require discussion, and they will be approached in the order shown in Table 1.

1. Crankcase Gas Samples for HC, CO, CO_2, and NO_x

Crankcase gas samples were taken direct for HC analysis and in bags for CO, CO_2, and NO_x analysis. Direct sampling is essential for HC from diesels due to the need to measure at 190°C, and concentrations of the other gases were low enough to permit bag sampling. Direct sampling would have been employed for all the gases, but total continuous flowrates for all the analyzers combined exceeded the output from the crankcase of the development engine in some operating modes. Tedlar* sample bags were filled using a Metal Bellows pump which pulled gases from the crankcase vent and through a glass fiber filter.

To document gas flowrates from the engines' crankcases and to permit mass rate computations for gaseous constituents, measurements were taken on both 6V-71 engines with the system shown schematically in Figure 1. Using the pump to scavenge the system prevented the crankcase vent from seeing any increase in backpressure, thereby making the flow measurements as accurate as possible.

Crankcase flowrates from the NTC-350 engine were too high, under some operating conditions, to use the dry gas meter system just described. The alternative adopted was to use the dilution system designed for impactor studies as a measurement device. This system is shown schematically in Figure 2 as set up for dilution/impactor work. When used to measure blowby rate, the dilution air inlet and the sample outlet were capped; and the blower speed was adjusted to preserve atmospheric pressure at the crankcase outlet. The orifice downstream of the blower provided the flow measurement, having been calibrated against a laminar flow element.

In addition to providing input data to pollutant mass flow calculations where concentrations were measured by mode, the modal crankcase flowrates also provided a basis for proportional sampling of other constituents during

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* registered trademark of E. I. duPont De Nemours & Company.

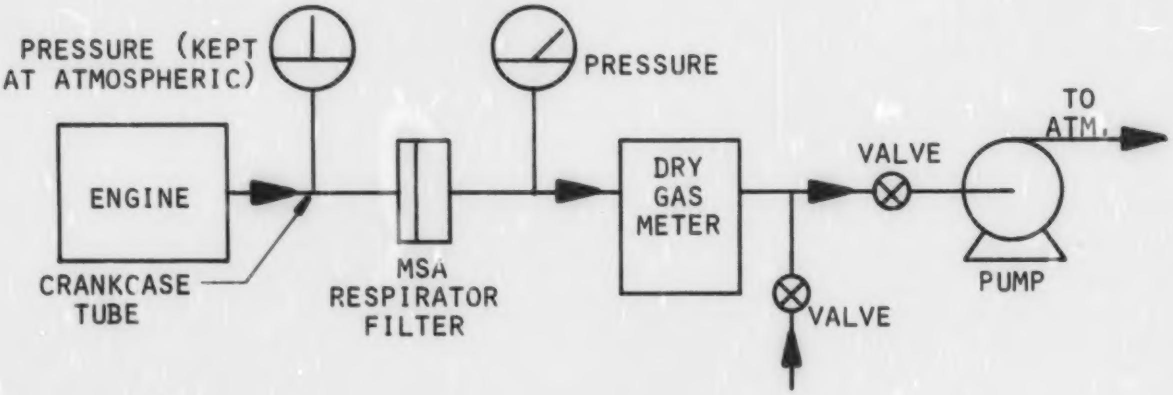
PRESSURE (KEPT AT ATMOSPHERIC)
PRESSURE
TO ATM.
ENGINE
DRY GAS METER
VALVE
CRANKCASE TUBE
MSA RESPIRATOR FILTER
VALVE
PUMP

FIGURE I. CRANKCASE EMISSION FLOW MEASUREMENT SYSTEM

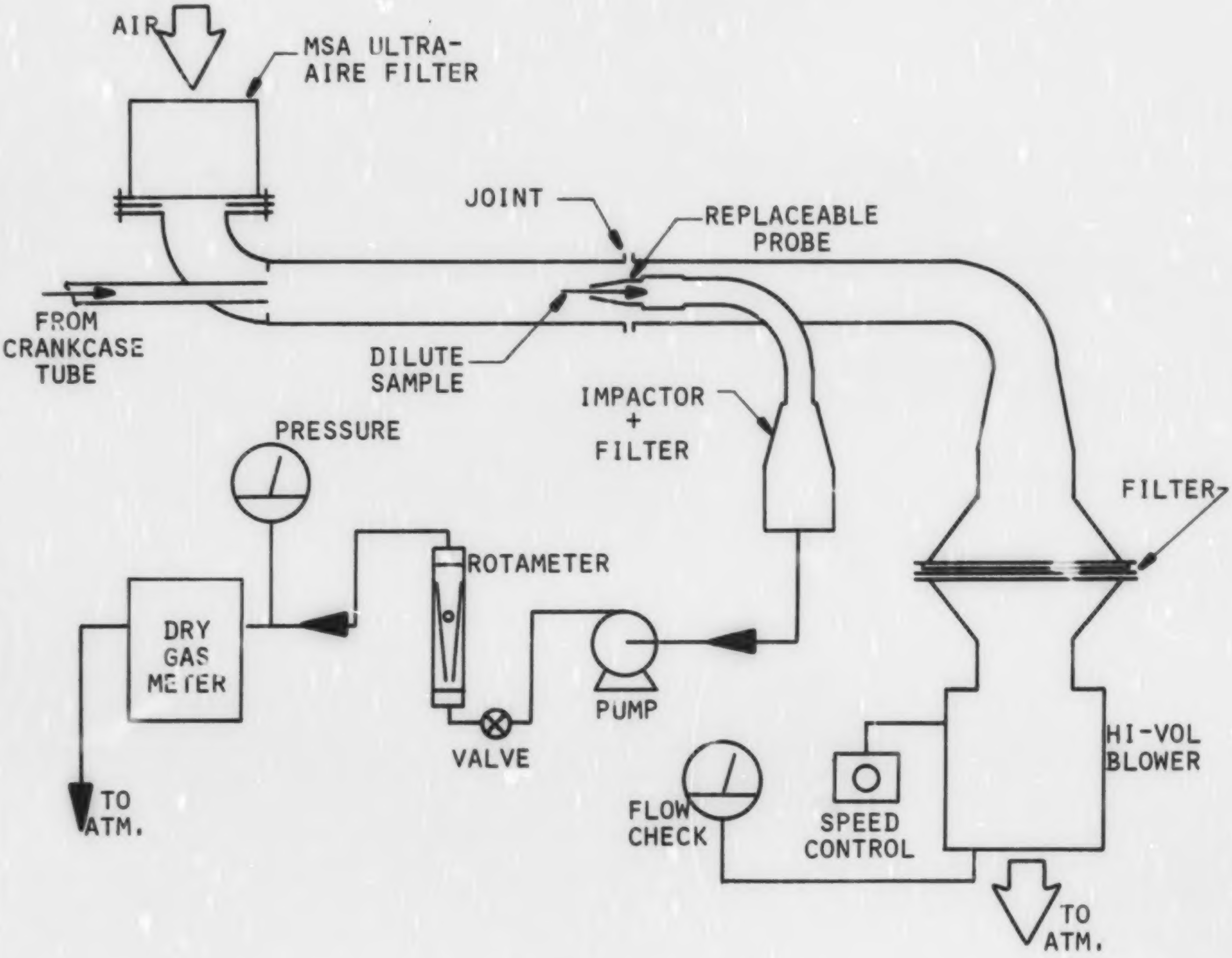
AIR
MSA ULTRA-AIRE FILTER
JOINT
REPLACEABLE PROBE
FROM CRANKCASE TUBE
DILUTE SAMPLE
IMPACTOR + FILTER
PRESSURE
FILTER
ROTAMETER
DRY GAS METER
PUMP
VALVE
HI-VOL BLOWER
FLOW CHECK
SPEED CONTROL
TO ATM.
TO ATM.

FIGURE 2. SAMPLING/DILUTION SYSTEM FOR IMPACTOR STUDIES

composite runs. The maximum flowrate for a given sampling system was used during the mode in which the engine emitted its maximum flow, and sampling rates during the other modes were set proportionately lower. "Composite" flowrates were computed by time-weighting individual mode flowrates in the same way as the Federal 13-mode test(3) is time-weighted, then taking an average.

2. Crankcase Gas Samples for Aldehydes and Individual Hydrocarbons

Samples for aldehyde analysis by DNPH(4) were taken directly from the blowby outlet using the system shown schematically in Figure 3. The sample line was heated as far as the impingers. Maximum flowrate sampled was about 4 liters per minute, and flow through the system was held in constant proportion to total crankcase flow. The amount of DNPH reagent used in each impinger was 40 ml. In practice, samples for aldehyde analysis were usually taken concurrently with those for individual hydrocarbons. The system used to collect samples for individual HC analysis(5) is shown in Figure 4, and it also operated with a maximum flowrate of 4 liters per minute. Background air samples were taken concurrently with selected runs.

A gas chromatograph procedure was used to measure the individual hydrocarbon content of samples collected in the Tedlar bags. The chromatograph procedure employed a flame ionization detector and used a four-column arrangement in conjunction with dual gas sampling valves. The valves were pneumatically operated and could be sequenced electrically to operate in either the automatic or manual mode. All blowby chromatograms were obtained automatically.

Injection from the bags used for individual HC analysis to the chromatograph was through an ice water (0°C) trap. The trap was employed to retain other crankcase gaseous species which had earlier been found to interfere with and obscure the benzene and toluene chromatograms.

3. Crankcase Particulate Sampling Techniques

Particulate in crankcase flow was measured by several methods, the first of which was the sampler shown in Figure 5. This sampler collected all the crankcase particulate on a rectangular 203 mm x 254 mm (8 x 10 in) glass fiber filter. The filter was weighed before and after sampling under controlled conditions to determine the amount of particulate emitted. No attempt was made during sampling to maintain the crankcase outlet pressure exactly at atmospheric due to the "constant volume" procedure employed. This unit was called the "hi-vol" sampler due to its use of filters designed for hi-volume ambient samplers, and the particulate collected was used for several types of analysis discussed later. Dilution air was cleaned up using a 99.99+ % DOP-efficient "Ultra-Aire" filter.

Another measurement technique used was the dilution tunnel-impactor system shown earlier in Figure 2. In this system, the individual collection discs and the final filter in the impactor constituted the collection apparatus, and the other filter was used only to protect the blower. The dilution system was utilized so the impactor could be operated at a constant flowrate, which is necessary for obtaining an accurate size distribution. Total particulate collected with the impactor was determined by summing the amounts on each individual collection disc and the backup filter. Glass fiber collection discs

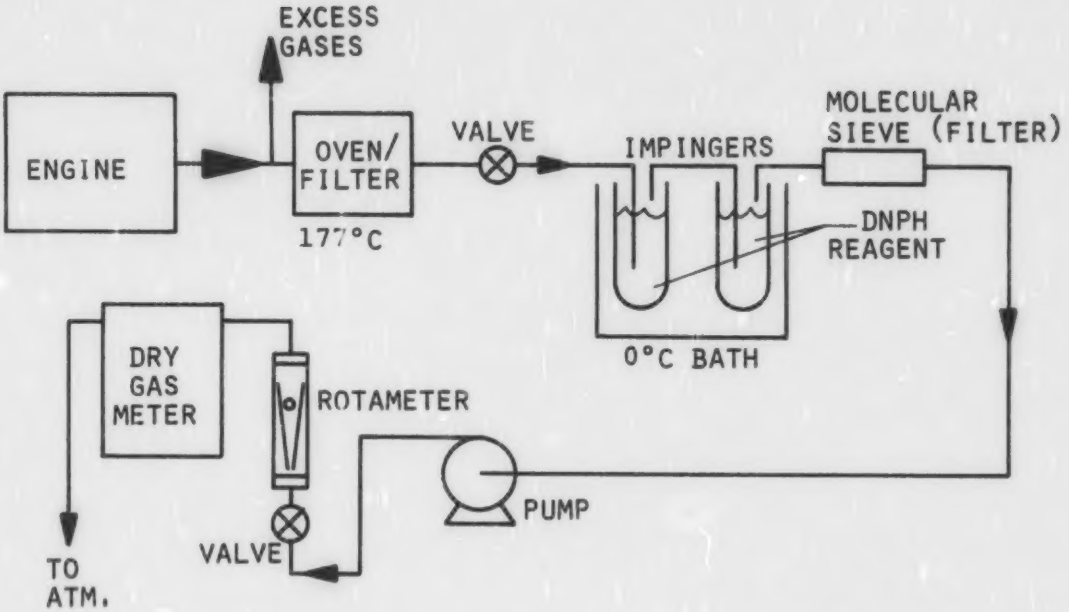
EXCESS GASES
ENGINE
OVEN/ FILTER
177°C
VALVE
IMPINGERS
MOLECULAR SIEVE (FILTER)
DNPH REAGENT
0°C BATH
DRY GAS METER
ROTAMETER
PUMP
VALVE
TO ATM.

FIGURE 3. SYSTEM FOR COLLECTION OF CRANKCASE GAS SAMPLES FOR ALDEHYDE ANALYSIS

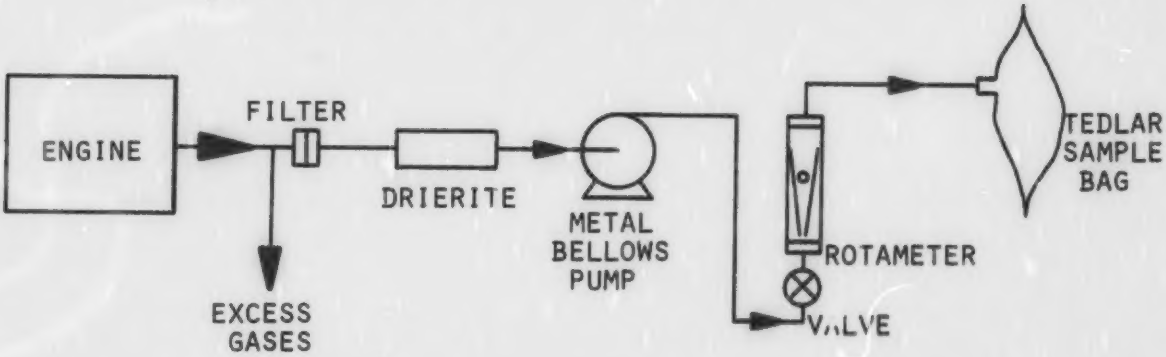
ENGINE
FILTER
DRIERITE
METAL BELLOWS PUMP
EXCESS GASES
ROTAMETER
VALVE
TEDLAR SAMPLE BAG

FIGURE 4. SYSTEM FOR COLLECTION OF CRANKCASE GAS SAMPLES FOR INDIVIDUAL HC ANALYSIS

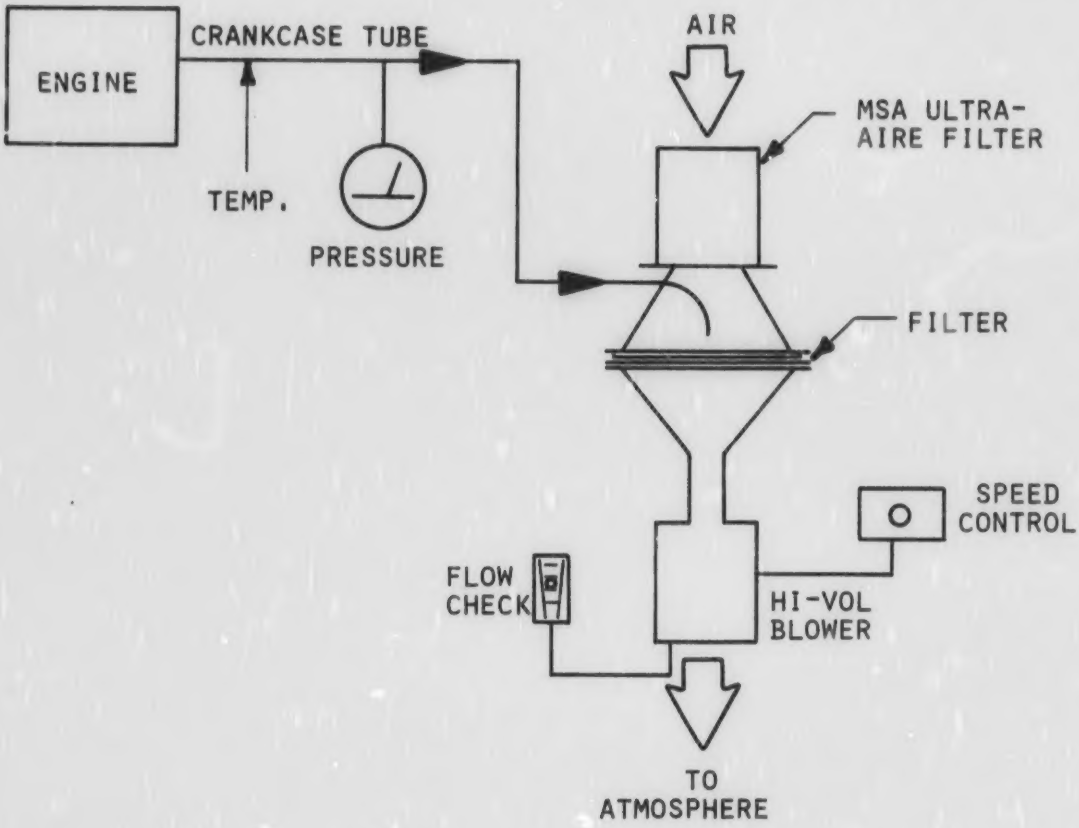
ENGINE
CRANKCASE TUBE
TEMP.
PRESSURE
AIR
MSA ULTRA-AIRE FILTER
FILTER
SPEED CONTROL
FLOW CHECK
HI-VOL BLOWER
TO ATMOSPHERE

FIGURE 5. CRANKCASE EMISSION TOTAL PARTICULATE SAMPLER

were used for most of the testing, with stainless steel discs being used on a few runs with the intent of examining the collected material using a scanning electron microscope.

Constant total (diluted) flow was maintained by the hi-vol blower and speed control, and total flow could be adjusted to suit each engine by using an appropriate probe size and maintaining isokinetic conditions. Dilution air was cleaned by the "Ultra-Aire" filter shown. Nominal flow through the impactor was maintained at 16.1 liters per minute (0.75 CFM), and probe diameters available ranged from 6.35 to 12.7 mm (0.25 to 0.5 in). Dilution tunnel dimensions were 50.8 mm (2 in) outside diameter, 47.6 mm (1.875 in) inside diameter, and 0.56 m (22 in) straight length upstream of the probe tip. The tube carrying undiluted sample into the tunnel was 25.4 mm (1 in) O.D. and was connected to the crankcase outlet with the minimum possible length of 12.7 mm (0.5 in) O.D. teflon tubing.

The third and final particulate collection system was designed around the 47 mm filters needed for several analyses (CHN, trace elements, and sulfate). It is shown schematically in Figure 6. When the 47 mm system was tried on the development engine, it was found that the filters plugged too quickly to permit completing an entire run. Subsequent samples were, therefore, obtained by sampling from the dilution tunnel (described above) at the point where the impactor was normally connected. This technique proved quite effective and permitted a constant flowrate through the filters instead of modal adjustment to maintain proportional sampling.

Photographs of the three particulate sampling systems described in this subsection are given as Figures 7 through 9, Figure 7 shows the "hi-vol" sampler connected to the 6V-71 development engine. Figure 8 shows the dilution tunnel/impactor system, and Figure 9 shows the 47 mm system connected to the dilution tunnel and operating with the 6V-71 bus engine.

4. Crankcase Particulate Appearance and Visual Sizing

This analytical technique was proposed to serve as a "calibration" of the impactor system. The plan was to obtain photos via SEM of portions of individual stage collection discs, and then to verify the range of particle sizes on each disc by examination of the photos. To permit good photos, special stainless steel collection discs were designed to replace the commercially-available glass fiber discs. They were procured from a photomachining company (Microphoto, Inc.). The discs were made of type 316 stainless steel and had a thickness of 0.051 mm (0.002 in). Tare weight per stainless steel disc was approximately 0.925 gram for the "A" type disc and 0.853 gram for the "B" type disc, as compared to 0.151 gram and 0.148 gram (respectively) for glass fiber. Both types of discs (A's were placed on odd stages and B's on even stages) are shown with their glass fiber counterparts in Figure 10. The stainless discs shown are unused (before sampling), and the glass fiber discs are used (they show different amounts of deposition). One glass fiber backup filter (final stage) as used in the impactor is also shown for comparison.

It was recognized at the outset that the SEM's operation in vacuum (1 x 10^{-5} mm Hg) might create problems with evaporation of some blowby particulate constituents if the stage were maintained at room temperature. It was decided, therefore, to construct a "cold stage" to support sections of the stainless discs in an attempt to keep the more volatile constituents of the particulate from evaporating. The cold stage is visible on the inside of a mock-up chamber door in Figure 11, insulated thermally from the door by a Teflon spacer. The stage was connected electrically by a very thin wire to ground, which is necessary for SEM operation. Also visible in Figure 11 is an insulated flask containing liquid N_2, which provided the cooling medium necessary to lower stage temperature to approximately -40°C. Temperature of the stage and sample were lowered by liquid N_2, while the chamber pressure was reduced. Actual stage temperature was measured by a thermocouple and a readout device while the SEM was in use. A wider view of the ETEC Autoscan Model U-1 SEM is given in Figure 12.

The SEM system as described proved unsuitable for crankcase particulate matter due to unforeseen complications. The first of these complications was

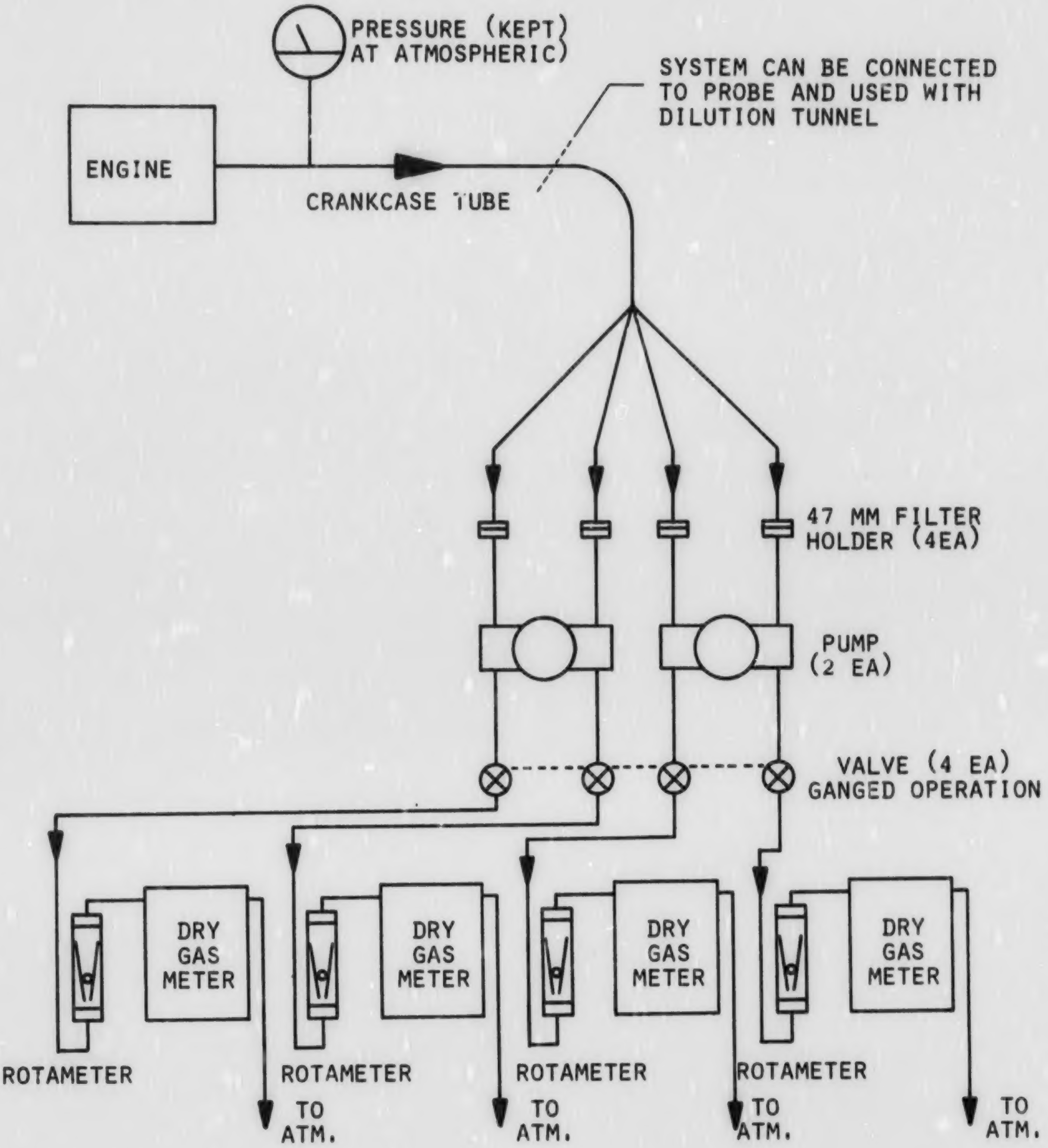
PRESSURE (KEPT AT ATMOSPHERIC)
SYSTEM CAN BE CONNECTED TO PROBE AND USED WITH DILUTION TUNNEL
ENGINE
CRANKCASE TUBE
47 MM FILTER HOLDER (4EA)
PUMP (2 EA)
VALVE (4 EA) GANGED OPERATION
DRY GAS METER
DRY GAS METER
DRY GAS METER
DRY GAS METER
ROTAMETER
ROTAMETER
ROTAMETER
ROTAMETER
TO ATM.
TO ATM.
TO ATM.
TO ATM.

FIGURE 6. SAMPLING SYSTEM FOR 47 MM FILTERS

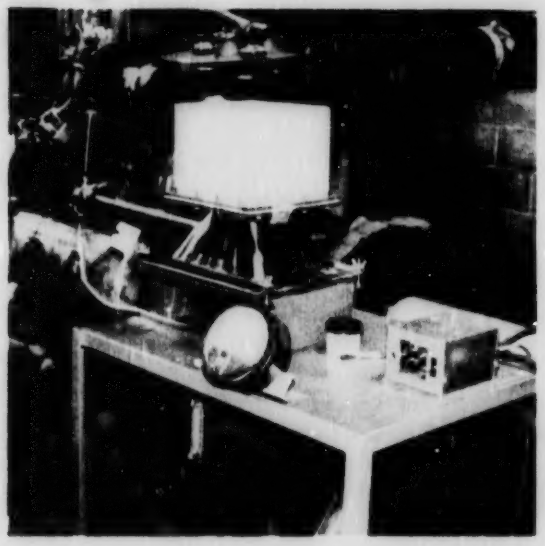

FIGURE 7. HI-VOL SAMPLER FOR TOTAL CRANKCASE PARTICULATE COLLECTION

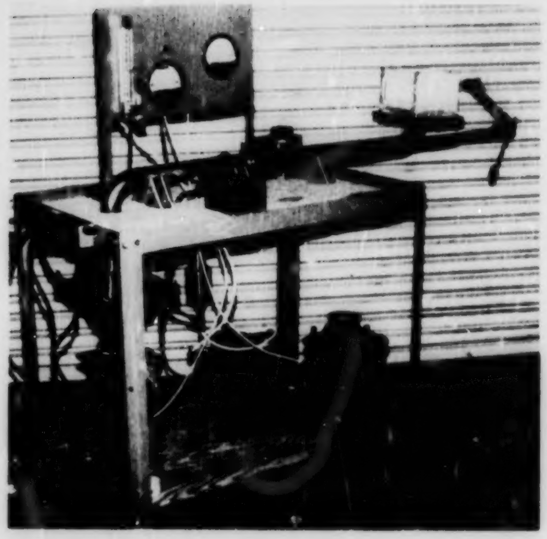

FIGURE 8. CRANKCASE PARTICULATE DILUTION TUNNEL FOR USE WITH IMPACTOR AND 47 mm SAMPLER

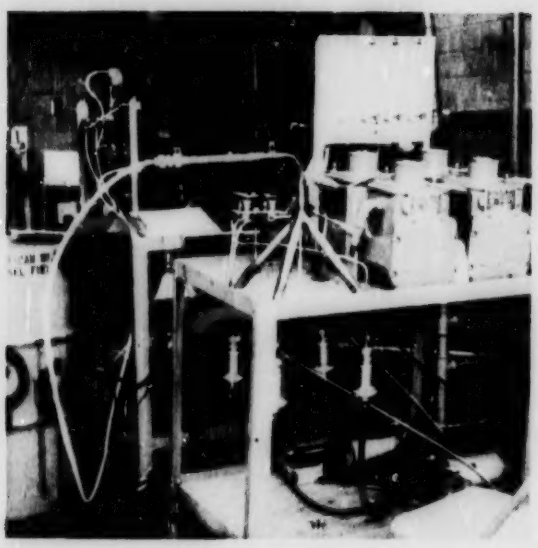

FIGURE 9. 47 mm SAMPLER FOR PARTICULATE COLLECTION

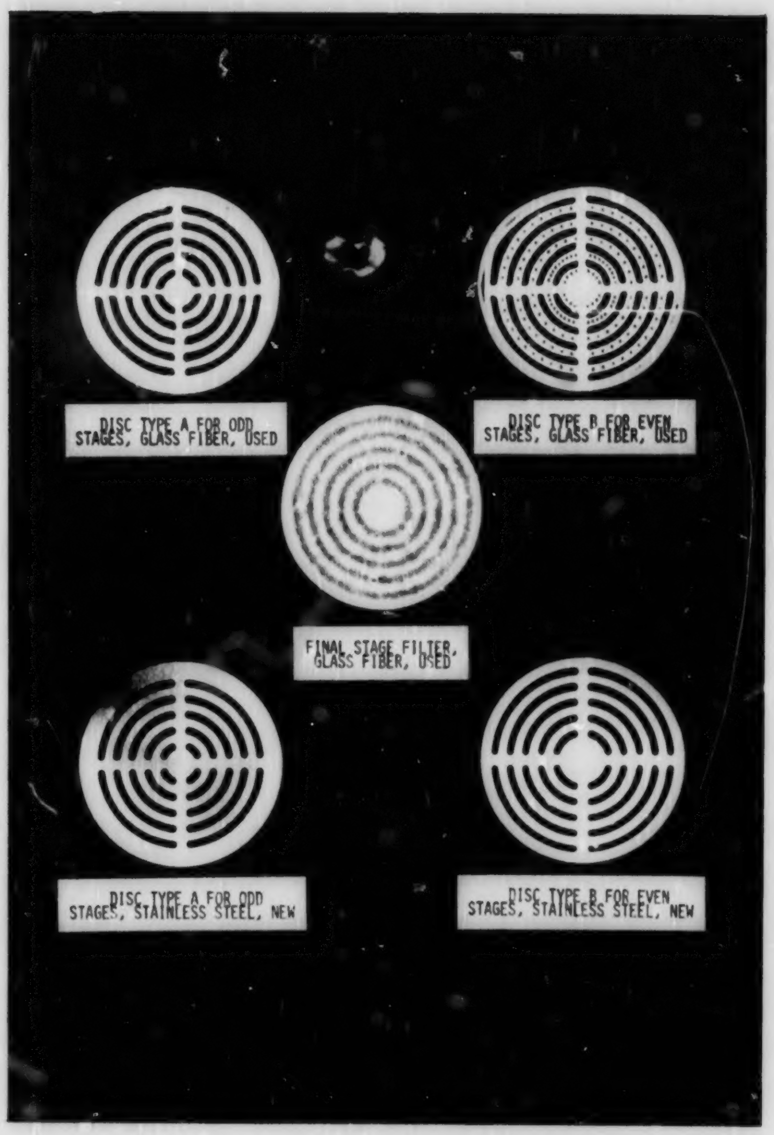
DISC TYPE A FOR ODD STAGES, GLASS FIBER, USED
DISC TYPE B FOR EVEN STAGES, GLASS FIBER, USED
FINAL STAGE FILTER, GLASS FIBER, USED
DISC TYPE A FOR ODD STAGES, STAINLESS STEEL, NEW
DISC TYPE B FOR EVEN STAGES, STAINLESS STEEL, NEW

FIGURE 10. DISCS AND FILTER USED IN PARTICLE SIZING IMPACTOR

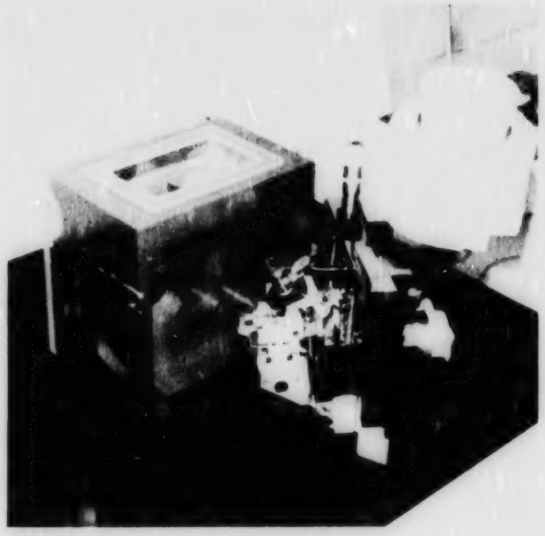

FIGURE 11. MOCK-UP SEM SAMPLE CHAMBER SHOWING COLD STAGE AND LIQUID NO_2 SYSTEM MOUNTED ON DOOR

FIGURE 12. GENERAL VIEW OF SEM

that the individual collected particles had agglomerated into continuous films, presumably while being collected, as shown in Figure 13 (800X at 5kV, 39°C). This agglomeration meant that individual particles were not resolvable. In addition, the electron beam caused local volatilization of the deposited material, leaving square "holes", with the surrounding material still at -40°C and thus too viscous to flow immediately into the holes. The results of making several scans at relatively high magnification are shown in Figure 14 (20X at 5kV, -39°C) as the square "holes" in the deposited films. When the SEM was operated at room temperature, the holes were not apparent. This result was presumably due to the deposit's flowing back into the areas from which material had been volatilized. Since the SEM technique was not developed further due to the problems mentioned above, it will not be discussed further as a part of other report sections.

5. Analysis of Particulate for Carbon, Hydrogen, Nitrogen, and Sulfur (CHNS)

The CHNS analysis was performed on samples collected by 47 mm glass fiber filters. Analytical work was done by Galbraith Laboratories, using automated thermal conductivity analysis of combustion products following combustion of whole filters. Data were reported as percentages of total particulate on the filter (particulate weight was supplied to the commercial lab) and were corrected for blank filter results. All samples analyzed were "composites" of the 13-mode procedure. This portion of the analysis was conducted using procedures developed under Contract No. 68-02-1230.(1)

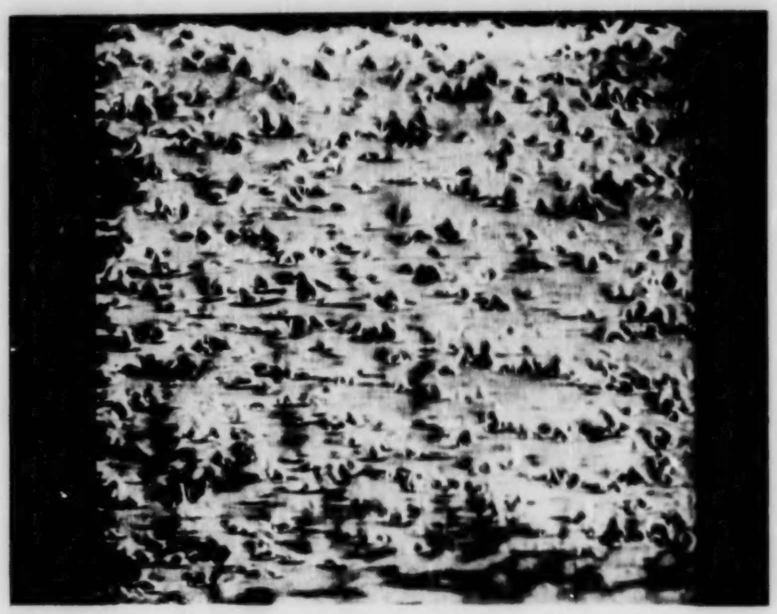

FIGURE 13. DIESEL CRANKCASE PARTICULATE DEPOSIT AT 800X, 5kV, AND -39°C; INDIVIDUAL PARTICLES NOT RESOLVED DUE TO COALESCING OF LIQUID AEROSOL

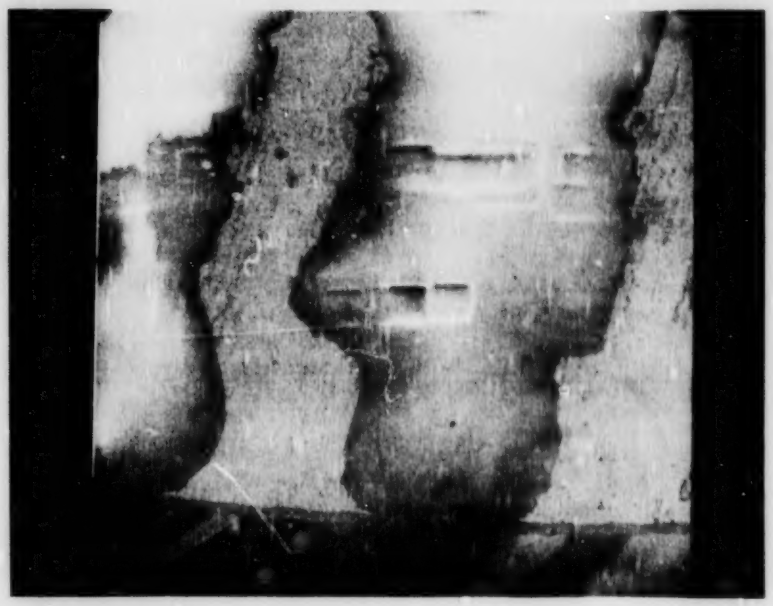

FIGURE 14. FILM OF DIESEL CRANKCASE PARTICULATE AT 20X, 5kV, AND -39°C SHOWING EFFECTS OF HIGH-MAGNIFICATION EXAMINATION OF SEVERAL SMALL AREAS

6. Analysis of Particulate for Metals and Other Elements

This elemental analysis was performed by the Institute's Mobile Energy Division using X-ray fluorescence. Filters used were 47 mm Fluoropore* discs, which were selected for low background metal content. Elements found in the particulate matter included phosphorus, chlorine, iron, zinc, and sulfur. The technique itself was capable of detecting and analyzing all the elements having atomic number 11 or greater, but no others were detected.

7. Analysis of Particulate for Sulfate

Sulfate samples collected on 47 mm fluorocarbon membrane (Fluoropore) filters were analyzed using the barium chloranilate procedure.(6) This procedure calls for ammonia treatment of the filters to assure conversion of sulfuric acid particulate into ammonium sulfate. Conversion to the stable ammonium salt improves the precision of the sulfate measurement by minimizing losses from the filter surface.

The filter samples were placed face up in their opened plastic cases in an ammoniation box. The box was evacuated and ammonia, bubbled from concentrated ammonium hydroxide, was allowed to fill the box. After a one-hour ammoniation period, the soluble sulfates were extracted from the filters. To begin this procedure, each filter was placed in a capped polypropylene bottle to which a 10 ml aliquot of isopropyl alcohol (IPA) and 40 percent deionized distilled water was added. The bottle was then shaken vigorously to permit proper leaching of the soluble sulfates. A portion of the extracted sulfate sample was passed through a strong cation exchange resin column, then through a column packed with barium chloranilate where the sulfates precipitated out as barium sulfate. This reaction released colored chloranilate ions which were measured colorimetrically with a UV photometer at 310 nm.

8. Determination of Total Organic Solubles in Particulate

Total organic solubles were determined by Soxhlet extraction of samples collected on hi-vol glass fiber filters. The solvent used was benzene, and refluxing occurred at about 20 cycles per hour for four hours. This portion of the analysis was conducted using procedures developed under Contract No. 68-02-1230.(1)

9. Analysis of Organic Solubles for Benzo(α)Pyrene (BaP)

Analysis for BaP was conducted using a method developed under previous Contract No. 68-02-1230,(1) except that a 19:1 mixture of pentane and ethyl ether was used as the thin-layer chromatograph elutant. The change to the pentane:ethyl ether mixture made the analysis more specific for BaP, reducing interferences from other polynuclear aromatic compounds. This BaP technique has been supplanted by revised methods, however, since the subject work was conducted. Newer techniques generally produce lower values than those obtained in the subject tests, and these lower values are considered more accurate than higher ones.

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* registered trademark of Millipore Corporation

10. Determination of Boiling Range for Organic Solubles

Boiling range of organic solubles was determined using a gas chromatograph procedure, ASTM D-2887. The column used was packed with Dexsil 300, and the operating temperature range was approximately 100-600°C. Internal standards in the range of C_8 to C_{11} were used at about 20 percent concentration, and calibrations were performed using a C_5 to C_{40} standard mixture. This method was also used on the fuels and oils involved in the program for purposes of comparison.

III. DEMONSTRATION OF METHODOLOGY

Sampling and analytical methods discussed in Section II were demonstrated on a Detroit Diesel-Allison 6V-71 engine mounted on a 500 hp (373 kW) eddy current dynamometer stand. This engine will be referred to from this point on as the "6V-71 development engine". To summarize the demonstration, all the methodology achieved some degree of success except the SEM examination of crankcase particulate deposited on impactor discs. The problems experienced with the SEM work were discussed fully in Subsection II.B.4. Less serious problems occurred with some of the other analyses, and they will be discussed along with corresponding results.

A. Measurement of Crankcase Gas (Blowby) Flowrates

Crankcase gas flowrates from the 6V-71 development engine are given in Table 3, and they are in the expected range for such an engine which is in good condition. These crankcase flows represent about 0.26 to 0.39 percent of engine airflow at corresponding conditions, and they were measured using the system shown in Figure 1.

TABLE 3. CRANKCASE FLOWRATES, 6V-71 DEVELOPMENT ENGINE

Operating Condition		Flowrate		
Engine rpm	Load, %	Std. m^3/hr[a]	SCFM[a]	kg/hr[b]
440 (idle)	---	0.68	0.40	0.82
1260	0	1.8	1.0	2.1
	25	1.7	1.0	2.1
	50	1.9	1.1	2.3
	75	1.9	1.1	2.3
	100	1.9	1.1	2.3
2100	0	3.6	2.1	4.4
	25	3.7	2.2	4.4
	50	3.8	2.2	4.5
	75	4.2	2.5	5.0
	100	4.3	2.5	5.2
13-mode composite[c]		2.44		

[a] at p = 101.3 kPa and T = 21°C

[b] assuming gases have same density as air

[c] time-weighting of individual modes as specified in Federal 13-mode procedure(3)

B. Measurement of HC, CO, CO_2, NO_x, and O_2 in Crankcase Gases and Comparison to Gaseous Exhaust Emissions

Gaseous constituents of crankcase emissions from the 6V-71 test engine were measured, yielding the results shown in Table 4. These results can be combined with the flowrates given in Table 3 to calculate mass emission rates of gaseous constituents using the following equations:

g/hr HC $= 0.000484$ (ppm C) (M, kg/hr),
g/hr CO $= 0.000970$ (ppm CO) (M, kg/hr),
g/hr $CO_2 = 15.2$ (% CO_2) (M, kg/hr), and
g/hr $NO_2 = 0.00159$ (ppm NO_2) (M, kg/hr).

TABLE 4. GASEOUS CONSTITUENTS OF CRANKCASE EMISSIONS, 6V-71 DEVELOPMENT ENGINE

Operating Condition		HC,	CO,	CO_2,	NO_x,	O_2,
Engine rpm	Load, %	ppm C	ppm	%	ppm	%
440 (idle)	---	440	26	0.09	7.6	20.9
1260	0	460	25	0.08	4.5	20.9
	25	490	4	0.06	4.7	20.9
	50	510	4	0.06	4.6	20.9
	75	540	18	0.10	10.	20.8
	100	600	140	0.21	12.	20.8
2100	0	520	0	0.04	2.7	20.9
	25	550	4	0.07	3.8	20.9
	50	570	8	0.10	6.1	20.8
	75	560	10	0.20	13.	20.8
	100	590	40	0.28	20.	20.8

The assumptions inherent in the equations are (1) that the average molecular weight of gaseous crankcase emissions is the same as that of air, and (2) that the (hydrogen:carbon) ratio of hydrocarbons emitted is 2.0. These assumptions are essentially equivalent to those used in deriving similar equations for the Federal diesel engine emissions certification procedure. Mass emission rates thus calculated are given in Table 5. A mathematical composite has been computed which can be compared to 13-mode composite exhaust emissions from this test engine (also given in Table 3). This comparison reveals that crankcase HC emissions (gaseous form only) amount to about 1.4 percent of exhaust HC and that other crankcase emissions range from 0.005 to 0.03 percent of their counterparts in exhaust gases. Complete gaseous exhaust emissions data for this engine are given in Appendix B, pages B-2 and B-3.

C. Measurement of Individual Hydrocarbons in Crankcase Gases

Individual hydrocarbons and aldehydes were sampled at rates proportional to total crankcase flow in each mode. These sampling rates are summarized in Table 6, and the individual HC data are given in Table 7. Methane, ethylene, and propylene are seen to be present in the largest concentrations, but it seems likely that ambient (background) methane contributed to levels for that compound. Smaller or trace quantities were noted for ethane, acetylene, propane, benzene, and toluene.

TABLE 5. CRANKCASE GASEOUS EMISSIONS FROM 6V-71 DEVELOPMENT ENGINE

Operating Condition		Emissions in grams per hour			
Engine rpm	Load, %	HC	CO	CO_2	NO_x
440 (idle)	---	0.17	0.021	1.1	0.010
1260	0	0.47	0.051	2.6	0.015
	25	0.50	0.008	1.9	0.016
	50	0.57	0.009	2.1	0.017
	75	0.60	0.040	3.5	0.037
	100	0.67	0.31	7.3	0.044
2100	0	1.11	0	2.7	0.019
	25	1.17	0.017	4.7	0.027
	50	1.24	0.035	6.8	0.044
	75	1.36	0.048	15.	0.10
	100	1.48	0.20	22.	0.17
13-mode composite of crankcase emissions		0.77	0.062	5.7	0.041
13-mode composite of exhaust emissions		46.1	425.	52,600.	665.

TABLE 6. COMPARISON OF INDIVIDUAL HC AND ALDEHYDE SAMPLING RATES TO CRANKCASE EMISSION FLOWRATES FROM 6V-71 DEVELOPMENT ENGINE DURING 13-MODE (3 min/mode) STEADY-STATE RUNS

Operating Condition		Crankcase Emission Flow Rate, Std. m^3/hr^a	Sample Rate, ℓ/min
Engine rpm	Load, %		
440 (idle)	---	0.68	0.64
1260	2	1.8	1.60
1260	25	1.7	1.60
1260	50	1.9	1.94
1260	75	1.9	1.94
1260	100	1.9	1.94
440 (idle)	---	0.68	0.64
2100	100	4.3	4.00
2100	75	4.2	4.00
2100	50	3.8	3.52
2100	25	3.7	3.52
2100	2	3.6	3.36
440 (idle)	---	0.68	0.64

[a] at p = 101.3 kPa and T = 21°C

TABLE 7. DISTRIBUTION OF CRANKCASE GAS INDIVIDUAL HYDROCARBONS, 13-MODE COMPOSITE, 6V-71 DEVELOPMENT ENGINE

Constituent	ppm C				
	Run 1	Run 2	Run 3	Background	Avg. Net
Methane	4.3	3.4	3.7	3.3	0.5
Ethylene	2.4	1.5	1.4	tr[a]	1.8
Ethane	0.3	0.2	0.2	0.1	0.1
Acetylene	0.2	tr[a]	tr[a]	---	tr[a]
Propane	0.2	tr[a]	---	---	tr[a]
Propylene	2.2	1.3	1.2	---	1.6
Benzene	0.3	0.3	0.3	---	0.3
Toluene	tr[a]	---	tr[a]	tr[a]	---
Total non-Methane	5.8	3.3	3.1	0.1	3.8

[a] trace, less than 0.1 ppm C

D. Measurement of Aldehydes in Crankcase Gases

Aldehydes were measured in the blowby of the 6V-71 development engine by the DNPH method. The results of this analysis are summarized in Table 8, Run 1 having been discarded due to an apparent air leak in the sampling system. Problems encountered with this analysis include interferences from fuel and oil constituents which were collected along with the sample and which eluted at the same times as some of the DNPH derivatives. The DNPH procedure was originally intended for use on dilute exhaust from gasoline-powered vehicles, and further development would probably be necessary before it could be considered entirely reliable for use with either diesel exhaust or diesel crankcase flows.

TABLE 8. CRANKCASE GAS ALDEHYDE CONCENTRATIONS FOR THE 6V-71 DEVELOPMENT ENGINE, 13-MODE COMPOSITE

Date	Run	Concentration in mg/m^3[a]							
		Form-aldehyde	Acet-aldehyde	Acetone[b]	Isobutyr-aldehyde[c]	Croton-aldehyde	Hexanal	Benz-aldehyde	Total
5/4/76	2	0.68	0.93	1.4	1.9	1.3	1.6	1.3	9.1
5/4/76	3	2.0	1.8	1.8	2.4	ND[d]	0.60	0.24	8.8

[a] at p = 101.3 kPa and T = 21°C
[b] includes acetone, acrolein, and propanal
[c] includes isobutyraldehyde, n-butyraldehyde, and methyl ethyl ketone
[d] none detected

E. Particulate Mass Emissions by Three Techniques

Initial particulate sampling was performed using the hi-vol sampler, permitting the engine's entire crankcase flow to be diluted and filtered. These tests resulted in the data given in Table 9, showing good repeatability between 13-mode runs. The difference between particulate rates for the 11-mode and 13-mode procedures is due to the higher time-weighting factors given to the high-power modes in the 11-mode sequence.

TABLE 9. CRANKCASE PARTICULATE MASS EMISSIONS FROM 6V-71 DEVELOPMENT ENGINE, HI-VOL SAMPLER

Engine Operating Procedure	Filter No.	Particulate Weight, g	Particulate Mass Rate, g/hr	Particulate Concentration,[a] mg/m^3
11-mode composite[b]	AR-6001	0.686	1.03	----
	AR-6002	0.669	1.00	----
13-mode composite	AR-6003	0.533	0.820	336.
	AR-6004	0.501	0.771	316.
	AR-6005	0.514	0.791	324.
	AR-6006	0.485	0.746	306.
	AR-6007	0.486	0.748	307.
	AR-6008	0.554	0.852	349.
	AR-6010	0.538	0.925	379.
	AR-6011	0.527	0.811	332.
Average of 13-mode runs		0.517	0.796	331.

[a] at p = 101.3 kPa and T = 21°C
[b] initial runs conducted during exhaust particulate sampling tests

Another set of particulate rate data was obtained from test work using the 47 mm sampler for collection. This instrument collected samples on four filters simultaneously, two of the Fluoropore type and two of glass fiber. Data from these runs are summarized in Table 10, indicating reasonable run-to-run agreement. The average mass rate for the 47 mm filters was 0.70 gram per hour, and the average concentration was 288 mg/m^3. These figures are about 12 percent lower than those measured by the hi-vol sampler, which is the expected direction of change given the higher wall surface area per unit volume of sample which is characteristic of the 47 mm sampler.

The final set of particulate rate data was acquired using the impactor system, although the primary goal of the impactor evaluation was to determine particle size distribution. These data are given in Table 11, and the average mass rate and concentration were about 0.48 gram per hour and 196 mg/m^3, respectively. These values, even lower than those obtained using the 47 mm sampler, again reflect the sampler wall surface area per unit volume of sample. This unit in particular presents a number of opportunities for particles to adhere to surfaces other than those on which particulate was measured directly.

TABLE 10. CRANKCASE PARTICULATE MASS EMISSIONS FROM 6V-71 DEVELOPMENT ENGINE, 47 mm SAMPLER, 13-MODE COMPOSITE

	Filter Position					
	1			2		
	Filter No.	Particulate		Filter No.	Particulate	
Filter Type		g/hr	mg/m^{3a}		g/hr	mg/m^{3a}
Fluoropore	FH47-6006	0.66	271.	FH47-6007	0.67	274.
	FH47-6008	0.62	253.	FH47-6009	0.68	279.
	FH47-6010	0.70	285.	FH47-6011	0.69	284.
	FH47-6012	0.81	334.	FH47-6013	0.81	332.
	FH47-6014	0.68	279.	FH47-6015	0.67	273.

	Filter Position					
	3			4		
	Filter No.	Particulate		Filter No.	Particulate	
Filter Type		g/hr	mg/m^{3a}		g/hr	mg/m^{3a}
Glass fiber	A47-6006	0.68	280.	A47-6007	0.73	299.
	A47-6008	0.66	269.	A47-6009	0.76	314.
	A47-6010	0.77	315.	A47-6011	0.81	333.
	A47-6012	0.63	258.	A47-6013	0.59	240.
	A47-6014	0.74	301.	A47-6015	0.68	280.

[a] at p = 101.3 kPa and T = 21°C

TABLE 11. CRANKCASE PARTICULATE MASS EMISSIONS FROM 6V-71 DEVELOPMENT ENGINE, IMPACTOR SYSTEM, 13-MODE COMPOSITE

	Particulate	
Disc Set Number	g/hr	mg/m^{3a}
101	0.463	190.
102	0.399	164.
SS-106	0.569	233.

[a] at p = 101.3 kPa and T = 21°C

F. Size Distribution of Particulate

As already mentioned, size distribution was determined using an inertial impactor which sampled isokinetically from a diluted crankcase flow. The flowrate through the impactor was held constant at 21.2 liters per minute (0.75 CFM). Data on particulate collected by impactor stage are given in Table 12, showing good agreement between the runs using glass fiber collection discs. Data obtained using stainless steel collection discs are similar to those just discussed, but different enough to lead to suspicion that the particle retention characteristics of the two types of discs are somewhat different.

TABLE 12. CRANKCASE PARTICULATE SIZING DATA FOR 6V-71 DEVELOPMENT ENGINE, 13-MODE COMPOSITE

Impactor Stage Number	Min. Diam.[a] Collected, microns	Collected Weight by Set, mg			Percent Recovered by Set			Cumulative Percent by Set		
		101	102	SS106	101	102	SS106	101	102	SS106
filter	under 0.43	1.082	1.051	3.892	8.3	8.7	23.5	8.3	8.7	23.5
8	0.43	1.519	1.445	2.638	11.7	12.0	15.9	20.0	20.7	39.4
7	0.62	3.671	3.420	4.017	28.2	28.4	24.2	48.2	49.0	63.6
6	1.05	4.865	3.904	3.835	37.4	32.4	23.1	85.6	81.4	86.7
5	2.1	0.839	1.380	1.196	6.5	11.4	7.2	92.1	92.8	93.9
4	3.3	0.753	0.612	0.546	5.8	5.1	3.3	97.8	97.8	97.2
3	4.6	0.274	0.251	0.340	2.1	2.1	2.0	100.0	100.0	99.2
2	7.0	0.0	0.0	0.077	0.0	0.0	0.5	100.0	100.0	99.7
1	11.1	0.0	0.0	0.048	0.0	0.0	0.3	100.0	100.0	100.0

[a] "50 percent effective cutoff diameter" (ECD)

Visual inspection of the glass fiber discs after each run indicated extremely good definition of impact zones (see Figure 10), especially as the stage particulate size decreased. Deposits on the stainless steel discs were less well defined. The fact that no weights were obtained on stages 1 and 2 of both runs is perhaps somewhat misleading, since some very light deposits were noted on them. Difficulty was experienced in weighing these two discs in particular because the stage gaskets cut them along their outer perimeter, but the problem was not as pronounced with the other stages.

Graphical presentation of the impactor data is given in Figures 15 and 16, the former being a log-probability plot and the latter a semilog plot. In order to make maximum use of the data, the dependent variable has been defined as "percent of particulate below stage effective cutoff diameter (ECD)". This definition means that filter-collected particles can be included on the graph. Using data for disc set 101 as an example, 8.3 percent is plotted against 0.43 microns since that percentage was below the 0.43 micron (stage 8) ECD. Although the log-probability plot is a more standard form for impactor data, the semilog plot is also considered useful for crankcase particulate data.

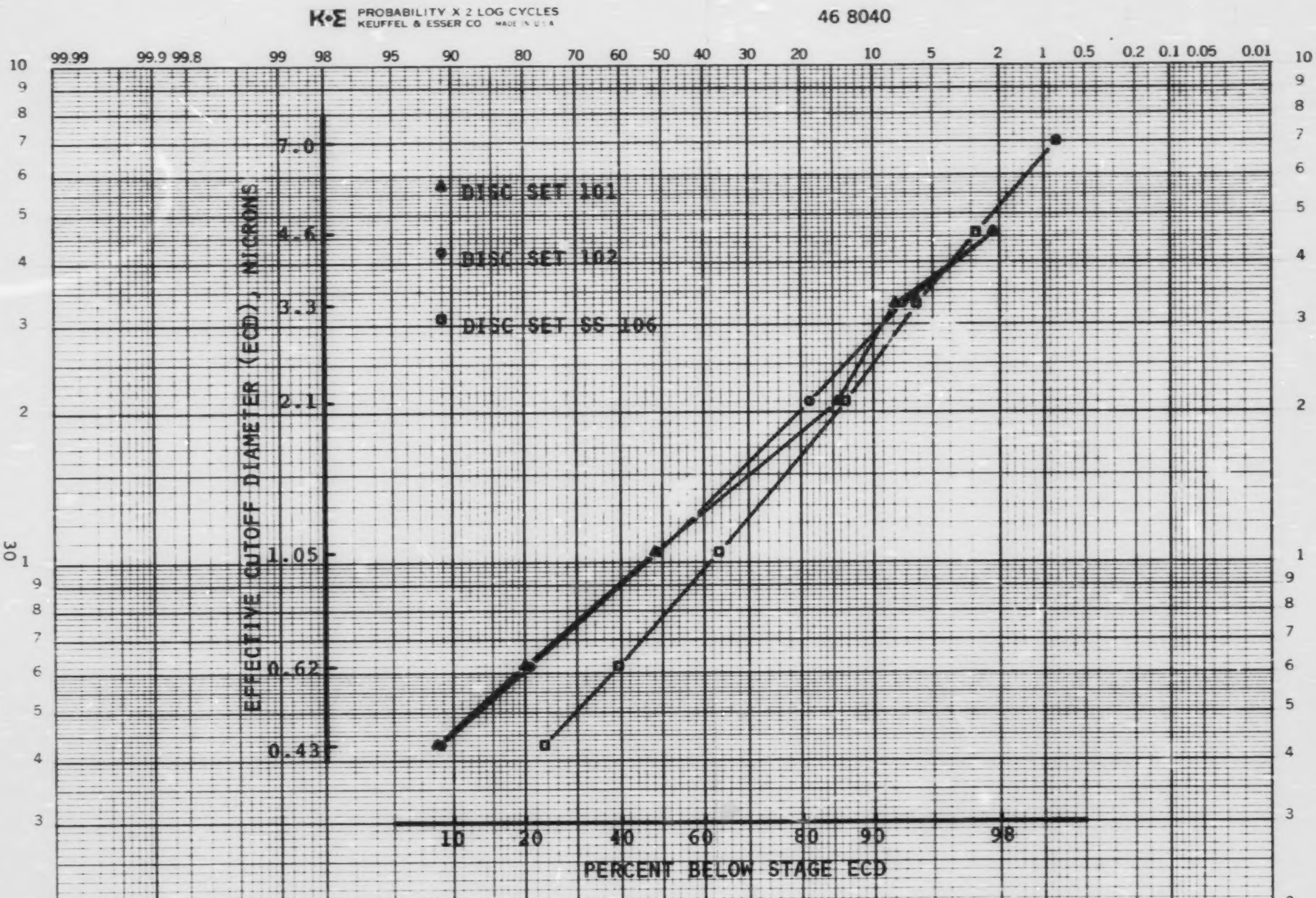

FIGURE 15. LOG-PROBABILITY PLOT OF 6V-71 DEVELOPMENT ENGINE CRANKCASE PARTICULATE SIZE DISTRIBUTION, 13-MODE COMPOSITE

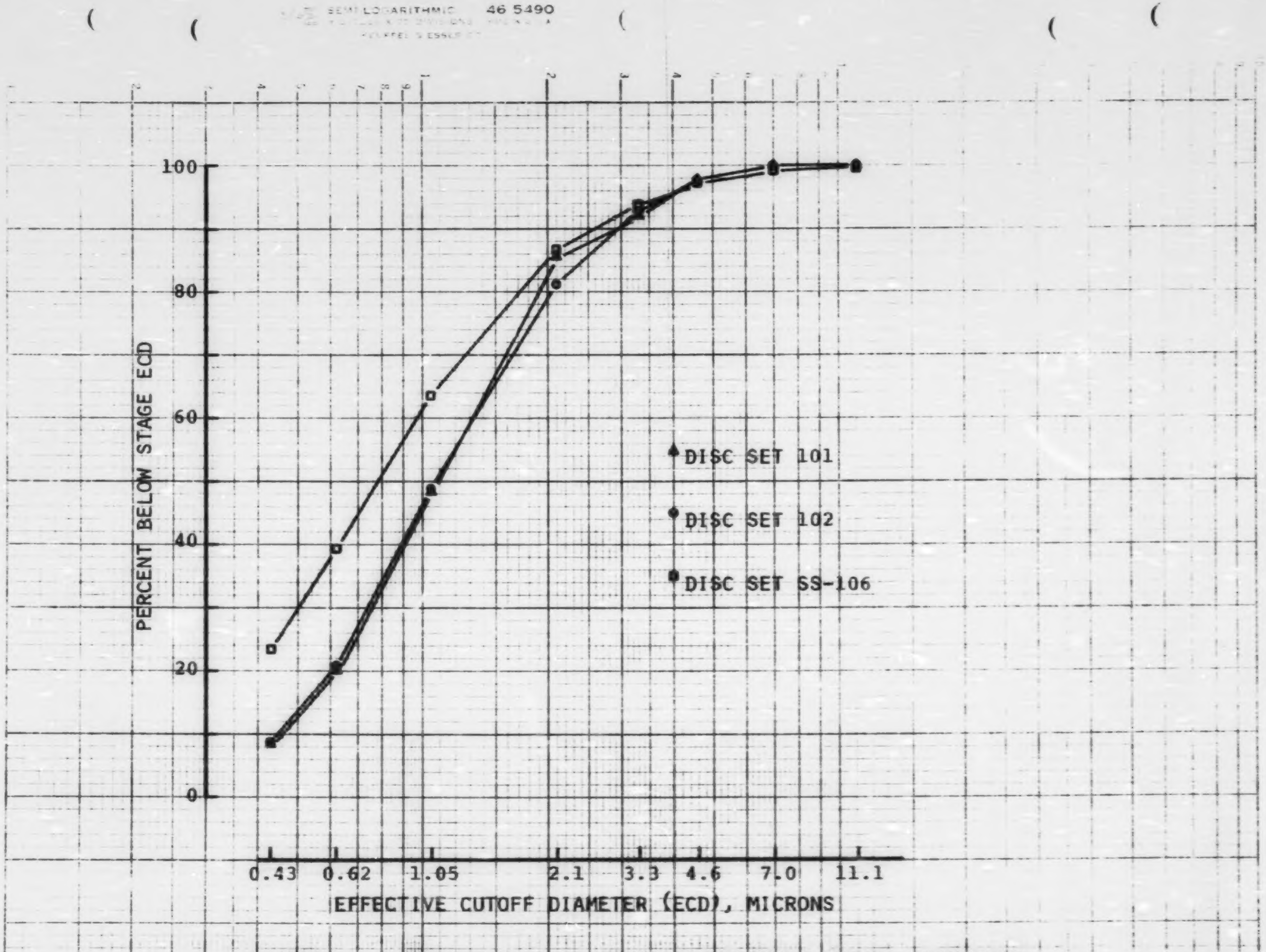

FIGURE 16. SEMILOG PLOT OF 6V-71 DEVELOPMENT ENGINE CRANKCASE PARTICULATE SIZE DISTRIBUTION, 13-MODE COMPOSITE

G. Amount and Boiling Point Distribution of Organic Solubles in Particulate

The amount of soluble organic material in the crankcase particulate matter was determined by Soxhlet extraction, and the boiling point distributions were determined by gas chromatography. Data on these properties are given in Table 13 along with boiling ranges on new and used lubricating oils. Approximately 88 percent of the particulate, on the average, was soluble. Solubles had somewhat lower initial boiling points than either new or used oils but were very similar to the oils in boiling range between 40 and 90 percent points. These data are certainly not conclusive, but they indicate a likelihood that the particulate was mainly oil-derived.

TABLE 13. AMOUNT AND BOILING RANGE OF SOLUBLES IN CRANKCASE PARTICULATE, 6V-71 DEVELOPMENT ENGINE, 13-MODE COMPOSITE

Filter No.	Particulate, g	Solubles, g	% Solubles	Boiling Range of Solubles Temperature in °C at Weight % Off								
				1	10	20	40	60	80	90	95	97
AR-6003	0.5535	0.4181	78.3	266	336	428	483	506	528	552	576	591
AR-6004	0.5006	0.4628	92.4	274	331	401	467	501	533	576	---	---
AR-6005	0.5144	0.4733	92.0	277	348	434	485	513	537	558	577	---
AR-6006	0.4850	0.4360	90.0	278	344	428	482	515	542	566	603	596
Average			88.2	274	340	423	479	509	535	563	585	594
New oil for comparison				311	436	465	491	515	545	578	627	660
Used oil for comparison				316	428	460	489	511	537	557	574	580

H. Benzo(α)Pyrene (or BaP) in Particulate Organic Solubles

Determination of BaP was conducted to provide an indication of polynuclear organic matter in the soluble fraction of particulate. These data are given in Table 14 for the development engine, expressed in several units. Computation of BaP in µg/hr was based on total BaP collected during each run of 39 minutes duration. Note that the analysis methodology used probably produced higher values than newer methods would have produced.

I. Elemental Composition of Particulate

This subsection includes data from two sources. Data on carbon, hydrogen, nitrogen, and sulfur by combustion were obtained by Galbraith Laboratories. Data on elements by X-ray fluorescence were obtained by the Mobile Energy Division, assisting the Department of Emissions Research on this project. The resulting information is summarized in Table 15, indicating a predominantly hydrocarbon composition with relatively small amounts of other elements. Carbon/hydrogen ratio of particulate is similar to that of used engine lubricating oil (6.38 versus 6.63, respectively). A measurable amount of sulfur was found by both X-ray and combustion, but the X-ray data are considered more reliable and accurate due to previous experience with both techniques.

TABLE 14. BaP CONTENT OF CRANKCASE PARTICULATE, 6V-71 DEVELOPMENT ENGINE, 13-MODE COMPOSITE[a]

Filter No.	Total BaP, µg	Weight % BaP in Particulate	Weight % BaP in Solubles	BaP µg/hr
AR-6003	22.7	0.0041	0.0054	35.
AR-6004	10.2	0.0020	0.0022	16.
AR-6005	11.4	0.0022	0.0024	18.
AR-6006	20.3	0.0042	0.0047	31.
Averages	16.2	0.0031	0.0037	25.

[a] technique used produced higher values than newer methods

TABLE 15. ELEMENTAL COMPOSITION OF CRANKCASE PARTICULATE, 6V-71 DEVELOPMENT ENGINE, 13-MODE COMPOSITE

	Weight % of Particulate by Combustion				
Filter No.(s)	C	H	N	S	Σ CHNS
A47-6006 & 07	86.2	13.1	0.09	0.4	99.8
A47-6008 & 09	86.2	13.1	---[a]	0.4	99.7
A47-6010 & 11	83.6	13.3	---[a]	0.7	97.6
A47-6012 & 13	83.6	13.4	---[a]	0.5	97.5
A47-6014 & 15	85.1	13.7	---[a]	0.8	99.6
Averages	84.9	13.3	---[a]	0.6	98.8

	Weight % of Particulate by X-ray				
Filter No.(s)	P	S	Cl	Fe	Zn
FP47-6007	0.04	0.43	0.02	-----[b]	-----[b]
FP47-6009	0.02	0.38	0.03	-----[b]	-----[b]
FP47-6011	0.03	0.37	0.02	0.0041	0.0044
FP47-6013	0.04	0.40	---[b]	-----[b]	-----[b]
FP47-6015	0.04	0.39	---[b]	-----[b]	-----[b]
Averages	0.03	0.39	0.01	-----[b]	-----[b]

[a] trace - less than 0.01 percent
[b] none detected

J. Sulfate ($SO_4^=$) in Particulate

Sulfate was measured by the BCA technique with the results shown in Table 16. Values determined were reasonably consistent compared with one another, and it can be computed that the sulfur in the sulfate made up about 12 percent of the total sulfur in the particulate as determined by X-ray. Data from the other engines tested will be examined on this point to see if the trend is uniform.

TABLE 16. SULFATE IN CRANKCASE PARTICULATE, 6V-71 DEVELOPMENT ENGINE, 13-MODE COMPOSITE

Filter No.	μg $SO_4^=$ on Filter	S in $SO_4^=$ as Weight % Particulate	$SO_4^=$, mg/hr
FH47-6006	4.8	0.040	0.80
FH47-6008	4.9	0.041	0.75
FH47-6010	5.4	0.045	0.93
FH47-6012	6.6	0.046	1.12
FH47-6014	6.0	0.051	1.03
Averages	5.6	0.045	0.93

IV. CHARACTERIZATION OF IN-SERVICE CUMMINS NTC-350 ENGINE

Characterization work was conducted on the two in-service engines described in Section II, and all the analytical methods were used except SEM studies. This section covers results achieved with the Cummins NTC-350 engine alone to avoid confusion which would result if data from the two engines were mixed.

A. Measurement of Crankcase Gas (Blowby) Flowrates

Measurement of crankcase emission flowrate on the truck NTC-350 diesel engine was accomplished using the flow measurement systems shown schematically in Figures 1 and 2. The system shown in Figure 2 was used during those modes for which blowby flows exceeded the flow capability of the system shown in Figure 1. The results, shown in Table 17, reflect inflow through the blowby tube observed at idle, 1500 - 2 percent load, and 2100 - 2 percent load, thereby obviating flow determinations at these modes. The negative pressures at the blowby tube ranged from 15 Pa at idle to 810 Pa at 2100 - 2 percent load. The proportional sample rates shown were used when samples were being taken for aldehydes and individual hydrocarbons. The crankcase flowrates from this engine were quite high as compared to those from the development engine, but it is not known whether or not they were typical of similar turbocharged engines. No published data on crankcase flows from a cross-section of engines have been located.

TABLE 17. CRANKCASE EMISSION FLOWRATES, TRUCK WITH NTC-350 ENGINE

Operating Condition		Crankcase Flowrate			Proportional
Engine rpm	Load, %	Std. m^3/hr[a]	SCFM[a]	kg/hr[b]	Sample, ℓ/min
600 (idle)	---	---[c]	---[c]	---[c]	0
1500	2	---[c]	---[c]	---[c]	0
1500	25	8.7	5.1	10.4	1.42
1500	50	13.0	7.6	15.5	2.11
1500	75	16.0	9.4	19.3	2.61
1500	100	21.3	12.5	25.5	3.46
2100	2	---[c]	---[c]	---[c]	0
2100	25	12.8	7.5	15.4	2.08
2100	50	17.2	10.1	20.6	2.79
2100	75	21.1	12.4	25.3	3.44
2100	100	24.6	14.5	29.5	4.00
Composite		10.8			

[a] at p = 101.3 kPa and T = 21°C
[b] assuming gases have same density as air
[c] zero flow or inflow

B. Measurement of HC, CO, CO_2, NO_x, and O_2 in Crankcase Gases and Comparison to Gaseous Exhaust Emissions

Gaseous constituents of crankcase emissions from the truck with NTC-350 engine were measured in three separate runs, and the average results are summarized in Table 18. These concentrations have been combined with the flowrates given in Table 17 to calculate mass emission rates of gaseous constituents, and the mass rates are given in Table 19. All the gaseous emissions were determined from 13-mode steady-state data. The composite exhaust emissions tabulated at the bottom of Table 19 for comparison were taken concurrently with the crankcase emissions. Comprehensive exhaust emissions data are given in Appendix B, pages B-4 through B-6. Comparison of crankcase and exhaust emissions reveals the crankcase (gaseous) HC amount as about 4.1 percent of exhaust HC and that other crankcase emissions range from about 0.08 to 0.43 percent of their counterparts in exhaust gases.

TABLE 18. GASEOUS CONSTITUENTS OF CRANKCASE EMISSIONS, TRUCK WITH NTC-350 ENGINE (AVERAGE OF THREE RUNS)

Operating Condition		HC	CO	CO_2	NO_x	O_2
Engine rpm	Load, %	ppm C	ppm	%	ppm	%
600 (idle)	---[a]	---	---	----	---	----
1500	2[a]	---	---	----	---	----
	25	81	27	0.30	35.	20.8
	50	84	110	0.29	46.	20.8
	75	99	335	0.35	57.	20.8
	100	164	597	0.38	61.	20.8
2100	2[a]	---	---	----	---	----
	25	70	75	0.33	37.	20.8
	50	73	76	0.34	63.	20.8
	75	91	79	0.36	44.	20.8
	100	105	118	0.43	37.	20.8

[a] zero flow or inflow

C. Measurement of Individual Hydrocarbons in Crankcase Gases

Samples for individual HC analysis were taken in proportion to crankcase gas flows, using the sampling rates given in Table 17. The results of these tests are summarized in Table 20. Concentrations above 3.0 ppm C were found for methane and ethylene. Propylene and benzene concentrations averaged just under 3.0 ppm C; while ethane, acetylene, and toluene averaged under 2.0 ppm C. Propane was indicated in trace quantities only. These concentrations were generally somewhat higher than those found in the crankcase gases of the 6V-71 development engine.

TABLE 19. CRANKCASE MASS EMISSIONS FROM TRUCK WITH NTC-350 ENGINE

Operating Condition		Emissions in grams per hour			
Engine rpm	Load, %	HC	CO	CO_2	NO_x
600 (idle)	---	-----	------	-----	-------
1500	2	-----	------	-----	-------
	25	0.41	0.27	47.6	0.58
	50	0.63	1.66	68.5	1.14
	75	0.92	6.26	102.	1.74
	100	2.03	14.77	147.	2.47
2100	2	-----	------	-----	-------
	25	0.52	1.12	77.1	0.90
	50	0.73	1.52	106.	1.44
	75	1.12	1.94	139.	2.54
	100	1.50	3.38	193.	3.52
13-mode composite of crankcase emissions		0.63	2.48	70.4	1.15
13-mode composite of exhaust emissions		15.3	582.	86,500	1170.

TABLE 20. CRANKCASE GAS INDIVIDUAL HYDROCARBONS,
13-MODE COMPOSITE, NTC-350 ENGINE

Constituent	ppm C				
	Run 1	Run 2	Run 3	Background	Avg. Net
Methane	8.8	5.1	4.2	2.7	3.3
Ethylene	10.4	5.6	5.0	tr[a]	7.0
Ethane	0.7	0.4	0.3	0.1	0.4
Acetylene	1.1	0.5	0.3	---	0.6
Propane	0.1	tr[a]	tr[a]	---	tr[a]
Propylene	4.0	2.4	2.4	---	2.9
Benzene	3.0	2.5	3.1	---	2.9
Toluene	2.8	1.6	1.1	---	1.8
Total non-Methane	22.1	13.0	12.2	0.1	15.6

[a] trace - less than 0.1 ppm C

D. Measurement of Aldehydes in Crankcase Gases

Aldehydes in the blowby gases of the NTC-350 engine were measured by the DNPH method, and the results are summarized in Table 21. Run 1 was discarded due to a calibration error, but runs 2 and 3 were valid and the results appear to agree quite well. These samples also contain a greater fraction of simple aldehydes as compared to those taken from the 6V-71 development engine. Some reservations must be expressed about the aldehyde data, as discussed earlier, because it was originally developed for dilute exhaust from gasoline-fueled vehicles.

TABLE 21. CRANKCASE GAS ALDEHYDE CONCENTRATIONS FOR THE NTC-350 TEST ENGINE, 13-MODE COMPOSITE

		Concentration in mg/m^{3a}							
Date	Run	Formaldehyde	Acetaldehyde	Acetone[b]	Isobutyraldehyde[c]	Crotonaldehyde	Hexanal	Benzaldehyde	Total
7/14/76	2	5.4	2.3	1.2	0.44	0.41	0.15	0.24	10.1
7/14/76	3	5.1	1.5	0.72	1.1	0.40	0.047	0.26	9.1

[a] at p = 101.3 kPa and T = 21°C
[b] includes acetone, acrolein, and propanal
[c] includes isobutyraldehyde, n-butyraldehyde, and methyl ethyl ketone

E. Crankcase Particulate Mass Emissions by Three Techniques

The first type of particulate measuring system used on the NTC-350 was the "hi-vol" system, which sampled the entire crankcase flow. The results of the hi-vol tests are presented in Table 22, showing good repeatability between runs. Concentration of particulate from this engine was lower than from the development engine, but crankcase flow was higher. These effects compensated for each other to the point that particulate mass flowrate from the NTC-350 was only about 27 percent higher than that from the development engine.

A second and independent set of particulate data was obtained from test results using the 47 mm sampler. These data are given as Table 23, and they show reasonable consistency and agreement with the hi-vol data. As averages, particulate rate was 1.03 grams per hour with the 47 mm sampler and particulate concentration was 95.8 mg/m^3. It was mentioned in the discussion of data on the development engine that particulate rate and concentration were expected to be somewhat lower using the 47 mm system as compared to the hi-vol system. Data on the NTC-350 did not bear out this expectation, and no reasons have been discovered for this result.

The final set of particulate rate data was acquired using the impactor system, even though the main purpose of the impactor tests was to define particle size distribution. Impactor rate data are given in Table 24, and they average about 0.76 grams per hour and 71 mg/m^3. These values are about 25 percent lower than those obtained with either the hi-vol or the 47 mm systems, which is the expected direction of change.

TABLE 22. CRANKCASE PARTICULATE MASS EMISSIONS FROM AN NTC-350 ENGINE, HI-VOL SAMPLER, 13-MODE COMPOSITE

Filter No.	Particulate Weight, g	Particulate	
		Mass Rate, g/hr	Concentration, mg/m^{3a}
AR-6012	0.644	0.991	91.8
AR-6013	0.623	0.958	88.7
AR-6014	0.638	0.982	90.9
AR-6015	0.617	0.949	87.9
AR-6017	0.589	0.906	83.9
AR-6018	0.625	0.962	89.1
AR-6019	0.637	0.980	90.7
AR-6020	0.695	1.07	99.1
AR-6021	0.812	1.25	116.
Averages	0.653	1.01	93.1

[a] at p = 101.3 kPa and T = 21°C

TABLE 23. CRANKCASE PARTICULATE MASS EMISSIONS FROM NTC-350 ENGINE, 47 mm SAMPLER, 13-MODE COMPOSITE

Date	Run No.	Particulate Rate by Filter Position[a], g/hr				Particulate Concentration by Filter Position[a,b], mg/m^3			
		1	2	3	4	1	2	3	4
7/9/76	1	1.02	0.75	1.13	1.09	94.4	69.4	105.0	101.0
7/9/76	2	1.00	1.02	0.94	1.05	92.4	94.2	87.5	97.2
7/9/76	3	1.06	0.79	1.15	1.13	98.4	72.9	107.0	105.0
7/12/76	4	0.99	0.97	1.38	0.98	91.7	90.3	128.0	90.9
7/12/76	5	0.96	0.99	1.18	1.06	88.8	92.3	110.0	98.8

[a] Fluoropore filters at positions 1 and 2, glass fiber at 3 and 4
[b] at p = 101.3 kPa and T = 21°C

TABLE 24. CRANKCASE PARTICULATE MASS EMISSIONS FROM NTC-350 ENGINE, IMPACTOR SYSTEM, 13-MODE COMPOSITE

Disc Set Number	Particulate	
	g/hr	mg/m^{3a}
103	0.886	82.0
104	0.663	61.4
105	0.580	53.7
108	0.920	85.2

[a] at p = 101.3 kPa and T = 21°C

F. Size Distribution of Particulate

Impactor samples for size distribution study were taken isokinetically from a diluted total crankcase flow, maintaining a constant sample rate of 21.2 liters per minute (0.75 CFM). Data on particulate collected by impactor stage are given in Table 25, and they show good agreement between tests on the basis of percentage collected. Graphical presentation of these results is given in Figures 17 and 18, the former being a log-probability plot and the latter a semilog plot. Again note that the dependent variable is "percent of particulate below ECD". Three of the runs yielded very similar plots (disc sets 104, 105, and 108), but the first run had quite a bit less particulate on discs 1 through 4 than did the other three. It is possible that cutting of discs by gaskets had some influence on the results.

G. Amount and Boiling Point Distribution of Organic Solubles in Particulate

The soluble fraction of the particulate was determined by Soxhlet extraction, and the boiling range by gas chromatograph. Data on these properties are given in Table 26 along with boiling ranges on new and used lubricating oils. About 93 percent of the particulate, on the average, was soluble. The solubles were very similar in boiling range; and as a group, they were similar to the oils between 40 and 90 percent points. Solubles were somewhat lower-boiling than oils between IBP and 40 percent points, but the opposite was true above the 90 percent point.

H. Benzo(α)Pyrene (or BaP) in Particulate Organic Solubles

BaP was determined as an indicator of total polynuclear organic matter in the soluble fraction of particulate. Data are given in Table 27 for the NTC-350 engine, expressed in several sets of units. Computation of BaP in μg/hr was based on total sample collected during each 39-minute run. Note that the analysis methodology used probably yielded BaP values which were high as compared to those which would have been generated by newer methods.

I. Elemental Composition of Particulate

This subsection includes X-ray data determined by the Institute's Mobile Energy Division and CHNS data obtained from Galbraith Laboratories. Elemental data are presented as Table 28, and they indicate a predominantly

TABLE 25. CRANKCASE PARTICULATE SIZING DATA FOR NTC-350 ENGINE, 13-MODE COMPOSITE

Impactor Stage Number	Minimum Diameter[a] Collected microns	Collected Weight by Set, mg				Percent Recovered by Set				Cumulative % by Set			
		103	104	105	108	103	104	105	108	103	104	105	108
filter	under 0.43	2.364	2.050	1.824	2.447	20.0	22.6	23.9	19.4	20.0	22.6	23.9	19.4
8	0.43	2.483	2.024	2.074	3.359	21.1	22.3	27.2	26.7	41.1	44.9	51.1	46.1
7	0.62	4.044	2.814	2.081	4.001	34.3	31.0	27.3	21.8	75.4	75.9	78.4	77.9
6	1.05	2.518	1.578	1.121	1.671	21.4	17.4	14.7	13.3	96.8	93.3	93.1	91.2
5	2.1	0.312	0.304	0.199	0.551	2.6	3.3	2.6	4.4	99.4	96.6	95.7	95.6
4	3.3	0.072	0.099	0.063	0.181	0.6	1.1	0.8	1.4	100.0	97.7	96.5	97.0
3	4.6	0.0	0.081	0.128	0.187	0.0	0.9	1.7	1.5	100.0	98.6	98.2	98.5
2	7.0	0.0	0.0	0.055	0.124	0.0	0.0	0.7	1.0	100.0	98.6	98.9	99.5
1	11.1	0.004	0.126	0.086	0.069	0.0	1.4	1.1	0.5	100.0	100.0	100.0	100.0

[a] "50 percent effective cutoff ciameter" (ECD)

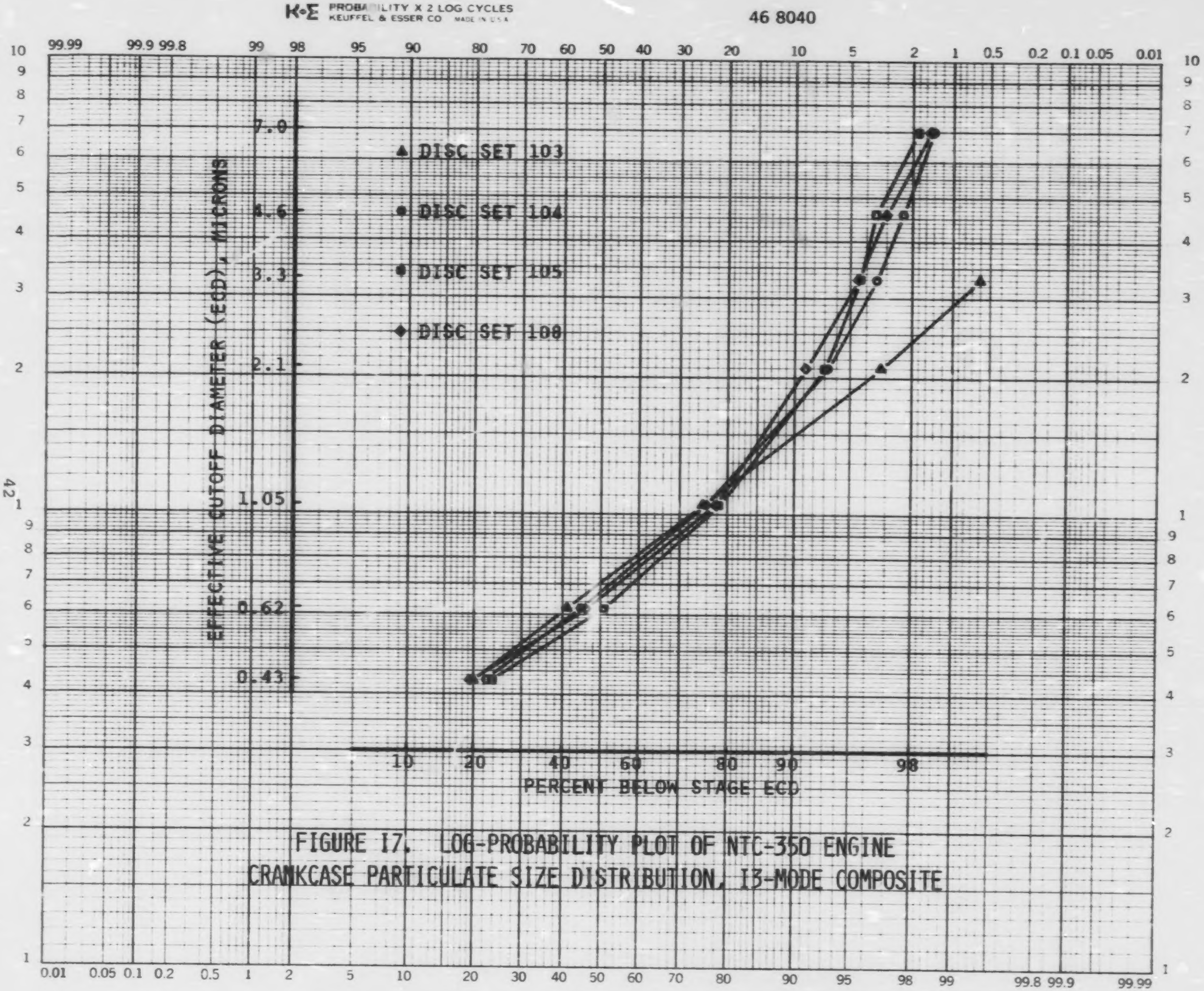

FIGURE 17. LOG-PROBABILITY PLOT OF NTC-350 ENGINE CRANKCASE PARTICULATE SIZE DISTRIBUTION, 13-MODE COMPOSITE

K+E SEMI LOGARITHMIC 46 5490
3 CYCLES X 70 DIVISIONS MADE IN U.S.A.
KEUFFEL & ESSER CO.

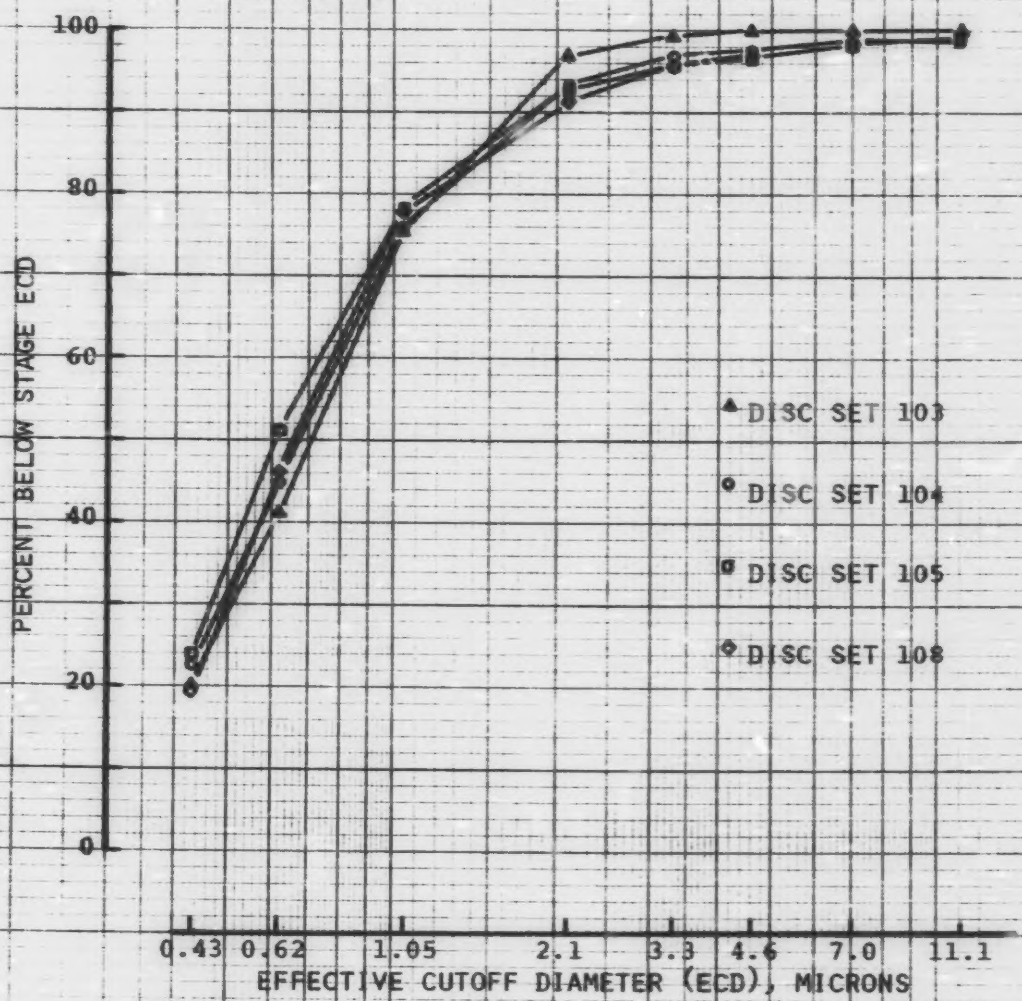

FIGURE 18. SEMILOG PLOT OF NTC-350 ENGINE CRANKCASE PARTICULATE SIZE DISTRIBUTION, 13-MODE COMPOSITE

TABLE 26. AMOUNT AND BOILING RANGE OF SOLUBLES IN CRANKCASE PARTICULATE, NTC-350 ENGINE, 13-MODE COMPOSITE

Filter No.	Particulate, g	Solubles, g	% Solubles	Boiling Range of Solubles Temperature in °C at Weight % Off								
				1	10	20	40	60	80	90	95	97
AR-6017	0.5890	0.5483	93.1	304	390	427	465	486	512	561	631	--[a]
AR-6018	0.6251	0.6016	96.2	313	385	424	460	483	507	538	602	622
AR-6019	0.6374	0.6116	96.0	303	391	427	464	482	503	519	543	568
AR-6020	0.6947	0.6132	88.3	303	396	437	468	486	506	533	585	636
AR-6021	0.8122	0.7440	91.6	298	389	419	460	481	506	533	596	--[a]
Averages			93.0	304	390	427	463	484	507	537	591	609
New oil for comparison				312	419	447	470	487	506	524	547	571
Used oil for comparison				311	416	446	471	490	511	536	566	--[a]

[a] out of range of analysis

TABLE 27. BaP CONTENT OF CRANKCASE PARTICULATE, NTC-350 ENGINE, 13-MODE COMPOSITE[a]

Filter No.	Total BaP, μg	Weight % BaP in Particulate	Weight % BaP in Solubles	BaP in μg/hr
AR-6017	1.4	0.00024	0.00026	2.2
AR-6018	6.3	0.00101	0.00104	9.7
AR-6019	1.8	0.00028	0.00029	2.7
AR-6020	13.9	0.00200	0.00227	21.4
AR-6021	9.6	0.00118	0.00129	14.8
Averages	6.6	0.00094	0.00103	10.2

[a] technique used produced high values as compared to newer methods

hydrocarbon material with relatively small amounts of other elements. A substantial amount of sulfur was found by both X-ray and combustion, but the X-ray data are considered to be more reliable. Carbon and hydrogen data are highly variable, and the low average carbon values are suspect because the resulting average C/H ratio by weight is very low (5.48 as compared to 6.49 for the engine's used lubricating oil). The only probable explanation for this result is that some contaminant in the solubles from particulate created a negative interference with the carbon analysis.

TABLE 28. ELEMENTAL COMPOSITION OF CRANKCASE PARTICULATE, NTC-350 ENGINE, 13-MODE COMPOSITE

	Weight % of Particulate by Combustion				
Filter Nos.	C	H	N	S	Σ CHNS
A47-6024 & 6025	68.4	12.1	---[a]	1.4	81.9
A47-6026 & 6027	81.4	15.0	0.09	1.4	97.9
A47-6028 & 6029	74.7	13.7	---[a]	1.0	89.4
A47-6034 & 6035	69.2	12.9	---[a]	3.0	85.1
Averages	73.4	13.4	0.02	1.7	80.6

Filter No.	Weight % of Particulate by X-ray			
	P	S	Cl	Fe
FH47-6026	---[b]	0.55	0.0	---[b]
FH47-6028	0.13	0.35	0.04	---[b]
FH47-6030	---[b]	0.39	---[b]	0.21
FH47-6034	---[b]	0.36	0.03	---[b]
FH47-6036	---[b]	0.41	0.05	---[b]
Averages	0.03	0.41	0.03	0.04

[a] trace - less than 0.01 percent

[b] none detected

J. Sulfate ($SO_4^=$) in Particulate

Sulfate was measured by BCA with results as shown in Table 29. The values were reasonably consistent, and it can be computed that the sulfur in the sulfate made up about 8 percent of the total particulate sulfur determined by X-ray. This percentage is lower than that for the development engine, which was 12 percent.

TABLE 29. SULFATE IN CRANKCASE PARTICULATE, NTC-350 ENGINE, 13-MODE COMPOSITE

Filter No.	μg $SO_4^=$ on Filter	S in $SO_4^=$ as Weight % Particulate	$SO_4^=$, mg/hr
FH47-6025	1.82	0.028	0.84
FH47-6027	2.63	0.040	1.21
FH47-6029	1.62	0.023	0.74
FH47-6033	2.14	0.034	1.00
FH47-6035	2.22	0.036	1.02
Averages	2.09	0.032	0.96

V. CHARACTERIZATION OF IN-SERVICE DETROIT DIESEL 6V-71 BUS ENGINE

Data on the 6V-71 development engine and the NTC-350 truck engine have already been presented in Sections III and IV, respectively. This section deals with data on the 6V-71 bus engine only, to prevent confusing data on the three engines.

A. Measurement of Crankcase Gas (Blowby) Flowrates

Where possible, within cost and time limitations, data were taken on the 6V-71 bus engine during two distinct types of 13-mode tests. One type used "standard" engine speeds of 2100 and 1260 rpm (plus idle), which are the speeds used to certify the 6V-71. The other type used "low" speeds of 1500 and 900 rpm, which are considered more representative of bus operation. All testing on the 6V-71 bus engine was performed using a No. 1 diesel fuel, while that on the NTC-350 and 6V-71 development engine was performed using a "national average" No. 2 diesel fuel.

Tables 30 and 31 give data on crankcase flowrates using both standard- and low-speed procedures, in addition to the proportional sample rates for individual hydrocarbon and aldehyde sampling (standard speeds). Although this engine was similar to the 6V-71 development engine, it had higher crankcase flows (by a factor of 1.6) and generally did not perform as well.

B. Measurement of HC, CO, CO_2, NO_x, and O_2 in Crankcase Gases and Comparison to Gaseous Exhaust Emissions

Gaseous constituents of crankcase emissions from the 6V-71 bus engine were measured in duplicate runs at both standard and low speeds. The average results are summarized in Tables 32 and 33. Concentrations given have been used with flowrates from Tables 30 and 31 to calculate mass emission rates of gaseous constituents. The results of these computations are given in Tables 34 and 35. Composite exhaust emissions tabulated at the bottoms of Tables 34 and 35 were derived from data taken concurrently with the crankcase gaseous emissions tests. Comprehensive exhaust emissions data are included in Appendix B, pages B-7 through B-10. Comparison of emissions from crankcase and exhaust shows that crankcase (gaseous) HC amounts to about 0.31 percent of exhaust HC at standard speeds and about 0.20 percent at low speeds. Other crankcase emissions ranged from about 0.04 percent to 0.08 percent of their counterparts in exhaust gases.

C. Measurement of Individual Hydrocarbons in Crankcase Gases

Samples for individual HC analysis were taken in proportion to crankcase gas flows, using the sampling rates given in Table 30. Results on these samples are summarized in Table 36, and they show slightly lower concentrations than the other 6V-71 engine did (the development engine). Only ethylene and propylene averaged over 1.0 ppm C, and all the other compounds are nearly in the trace category (0.2 ppm C or less).

TABLE 30. CRANKCASE EMISSION FLOWRATES, 6V-71 CITY BUS ENGINE AT STANDARD ENGINE SPEEDS

Operating Condition		Crankcase Flowrate			Proportional
Engine rpm	Load, %	Std. m^3/hr[a]	SCFM[a]	kg/hr[b]	Sample, ℓ/min
515 (idle)	---	1.2	0.7	1.4	0.71
1260	2	2.7	1.6	3.3	1.61
1260	25	2.9	1.7	3.5	1.71
1260	50	3.1	1.8	3.7	1.80
1260	75	3.1	1.8	3.7	1.83
1260	100	3.2	1.9	3.8	1.86
2100	2	5.6	3.3	6.7	3.27
2100	25	5.8	3.4	6.9	3.40
2100	50	6.2	3.6	7.4	3.63
2100	75	6.4	3.8	7.7	3.78
2100	100	6.8	4.0	8.1	4.00
Composite		3.9			

[a] at p = 101.3 kPa and T = 21°C

[b] assuming gases have same density as air

TABLE 31. CRANKCASE EMISSION FLOWRATES, 6V-71 CITY BUS ENGINE AT LOW ENGINE SPEEDS

Operating Condition		Crankcase Flowrate		
Engine rpm	Load, %	Std. m^3/hr[a]	SCFM[a]	kg/hr[b]
515	---	1.2	0.7	1.5
900	2	2.2	1.3	2.6
900	25	1.8	1.0	2.1
900	50	1.6	1.0	1.9
900	75	1.5	0.9	1.8
900	100	1.2	0.7	1.4
1500	2	3.6	2.1	4.4
1500	25	3.7	2.2	4.5
1500	50	3.9	2.3	4.7
1500	75	4.1	2.4	4.9
1500	100	4.3	2.5	5.1
Composite		2.5		

[a] at p = 101.3 kPa and T = 21°C

[b] assuming gases have same density as air

TABLE 32. GASEOUS CONSTITUENTS OF CRANKCASE EMISSIONS, CITY BUS 6V-71, STANDARD SPEEDS (AVERAGE OF TWO RUNS)

Operating Condition		HC	CO	CO_2	NO_x	O_2
Engine rpm	Load, %	ppm C	ppm	%	ppm	%
515 (idle)	---	258.	86.	0.45	23.5	20.7
1260	2	229.	37.	0.07	10.0	20.8
1260	25	242.	23.	0.15	29.0	20.7
1260	50	241.	39.	0.21	45.0	20.5
1260	75	299.	142.	0.40	71.5	20.2
1260	100	321.	695.	0.63	79.5	19.5
2100	2	285.	24.	0.11	28.5	20.7
2100	25	330.	21.	0.17	29.5	20.6
2100	50	336.	24.	0.30	50.0	20.4
2100	75	377.	41.	0.49	82.5	20.1
2100	100	319.	146.	0.66	91.5	20.0

TABLE 33. GASEOUS CONSTITUENTS OF CRANKCASE EMISSIONS, CITY BUS 6V-71, LOW SPEEDS (AVERAGE OF TWO RUNS)

Operating Condition		HC	CO	CO_2	NO_x	O_2
Engine rpm	Load, %	ppm C	ppm	%	ppm	%
515 (idle)	---	240.	109.	0.12	12.5	20.8
900	2	196.	33.	0.07	3.0	20.7
900	25	215.	24.	0.14	23.0	20.5
900	50	226.	123.	0.41	59.5	20.3
900	75	276.	341.	0.50	94.0	19.9
900	100	330.	1084.	0.66	80.0	19.5
1500	2	267.	32.	0.07	8.5	20.7
1500	25	299.	14.	0.14	32.0	20.5
1500	50	303.	33.	0.29	52.5	20.2
1500	75	336.	70.	0.45	70.5	20.1
1500	100	303.	416.	0.67	91.5	20.0

TABLE 34. CRANKCASE MASS EMISSIONS FROM CITY BUS 6V-71, STANDARD SPEEDS

Operating Condition		Emissions in grams per hour			
Engine rpm	Load, %	HC	CO	CO_2	NO_x
515 (idle)	---	0.18	0.12	9.8	0.05
1260	2	0.36	0.12	3.2	0.05
1260	25	0.41	0.08	7.7	0.16
1260	50	0.43	0.14	11.7	0.26
1260	75	0.54	0.51	22.7	0.42
1260	100	0.59	2.55	36.3	0.48
2100	2	0.92	0.16	10.6	0.30
2100	25	1.11	0.14	17.4	0.32
2100	50	1.20	0.17	33.1	0.59
2100	75	1.41	0.30	56.8	1.01
2100	100	1.26	1.15	81.1	1.18
13-mode composite of crankcase emissions		0.69	0.45	24.4	0.39
13-mode composite of exhaust emissions		220.	599.	47,900.	809.
crankcase/exhaust composite emissions, %		0.31	0.08	0.05	0.05

TABLE 35. CRANKCASE MASS EMISSIONS FROM CITY BUS 6V-71, LOW SPEEDS

Operating Condition		Emissions in grams per hour			
Engine rpm	Load, %	HC	CO	CO_2	NO_x
515 (idle)	---	0.17	0.15	2.5	0.03
900	2	0.25	0.08	2.6	0.01
900	25	0.22	0.05	4.5	0.08
900	50	0.21	0.23	12.1	0.18
900	75	0.24	0.59	13.6	0.27
900	100	0.22	1.46	14.0	0.18
1500	2	0.48	0.13	4.6	0.06
1500	25	0.65	0.06	9.5	0.23
1500	50	0.69	0.15	20.3	0.39
1500	75	0.79	0.33	33.1	0.55
1500	100	0.75	2.07	57.9	0.75
13-mode composite of crankcase emissions		0.39	0.44	14.3	0.22
13-mode composite of exhaust emissions		194.	774.	33,800.	625.
crankcase/exhaust composite emissions, %		0.20	0.06	0.04	0.04

TABLE 36. CRANKCASE GAS INDIVIDUAL HYDROCARBONS,
13-MODE COMPOSITE, 6V-71 BUS ENGINE (STANDARD SPEEDS)

Constituent	ppm C				
	Run 1	Run 2	Run 3	Background	Avg. net
Methane	2.5	3.4	3.4	3.0	0.1
Ethylene	1.6	2.0	1.9	tr[a]	1.8
Ethane	0.1	0.2	0.3	0.2	--[b]
Acetylene	0.2	tr[a]	--[b]	--[b]	0.1
Propane	tr[a]	0.2	0.2	tr[a]	0.2
Propylene	0.8	1.5	1.4	--[b]	1.2
Benzene	0.1	0.1	0.1	tr[a]	0.1
Toluene	0.1	0.1	0.1	0.1	--[b]
Total non-Methane	2.9	4.1	4.0	0.3	3.4

[a] trace - less than 0.1 ppm C
[b] below limit of detection

D. Measurement of Aldehydes in Crankcase Gases

Crankcase gases were analyzed for aldehydes by the DNPH method, and the results are summarized in Table 37. Run 1 was discarded due to anomalous results, thought to have been caused by an oil or other hydrocarbon interference. In terms of general ranges, aldehydes from the 6V-71 crankcase were similar to those from the other two engines. Consistency between runs, however, was not as good as that observed with the other two engines.

TABLE 37. CRANKCASE GAS ALDEHYDE CONCENTRATIONS FOR
THE 6V-71 BUS ENGINE, 13-MODE COMPOSITE (STANDARD SPEEDS)

	Run	Concentration in mg/m^3[a]							
		Formaldehyde	Acetaldehyde	Acetone[b]	Isobutyraldehyde[c]	Crotonaldehyde	Hexanal	Benzaldehyde	Total
9/1/76	2	3.2	2.1	1.7	2.6	0.68	0.77	0.81	11.9
9/1/76	3	3.8	3.3	2.7	3.5	1.4	3.4	ND[d]	18.1

[a] at p = 101.3 kPa and T = 21°C
[b] includes acetone, acrolein, and propanal
[c] includes isobutyraldehyde, n-butyraldehyde, and methyl ethyl ketone
[d] none detected

E. Crankcase Particulate Mass Emissions by Three Techniques

Initial particulate samples from the 6V-71 bus engine were taken with the hi-vol system, which collects particulate from the entire (diluted) crankcase flow. The results of these tests are summarized in Table 38, and they show good consistency. This engine had crankcase particulate concentrations almost twice as high as the 6V-71 development engine, and 6.7 times as high as the NTC-350 test engine. Consequently, the 6V-71 bus engine's crankcase particulate rate was about three times that of the 6V-71 development engine and about 2.5 times that of the NTC-350. These particulate rates also reflect the relatively high crankcase flowrates from the 6V-71 bus engine as compared to those from the 6V-71 development engine.

TABLE 38. CRANKCASE PARTICULATE MASS EMISSIONS FROM A 6V-71 BUS ENGINE, HI-VOL SAMPLER, 13-MODE COMPOSITE (STANDARD SPEEDS)

Filter No.	Particulate Weight, g	Particulate Mass Rate, g/hr	Particulate Concentration, mg/m³[a]
AR-6025	1.541	2.37	609.
AR-6026	1.558	2.40	617.
AR-6027	1.573	2.42	622.
AR-6028	1.641	2.52	648.
AR-6029	1.637	2.52	648.
AR-6030	1.581	2.43	625.
Averages	1.588	2.44	628.

[a] at p = 101.3 kPa and T = 21°C

Additional particulate rate and concentration data were obtained from tests using the 47 mm sampler, and this information is presented as Table 39. Values obtained show good consistency and reasonable agreement with hi-vol data given the differences in the sampling systems. Average particulate rate with the 47 mm system was 1.78 grams per hour, and average concentration was 459 mg/m^3. These values are about 25 percent lower than those obtained using the hi-vol system.

TABLE 39. CRANKCASE PARTICULATE MASS EMISSIONS FROM A 6V-71 BUS ENGINE, 47 mm SAMPLER, 13-MODE COMPOSITE

Date	Run No.	Particulate Rate by Filter Position[a], g/hr 1	2	3	4	Particulate Concentration by Filter Position[a,b], mg/m³ 1	2	3	4
8/26/76	3	1.59	1.64	1.63	1.65	409.	422.	419.	424.
8/27/76	1	1.82	1.81	1.94	2.08	468.	465.	499.	535.
8/27/76	2	----	----	1.85	1.83	----	----	476.	470.
8/27/76	4[c]	1.33	1.40	1.33	1.30	540.	566.	540.	526.
8/27/76	5[c]	1.32	1.37	1.37	1.36	536.	555.	555.	552.

[a] at p = 101.3 kPa and T = 21°C
[b] Fluoropore filters at positions 1 and 2, glass fiber at 3 and 4
[c] low speeds (900 and 1500 rpm) - others at standard speeds

In conjunction with particle sizing data, particulate rate information was obtained using the diluter-impactor system. Data from these tests indicates that a sample line leak was present, making the particulate rate data thus obtained of no value. Size distributions obtained in these runs have been scrutinized carefully for effects of sub-isokinetic sampling and erroneous impactor flowrates.

F. Size Distribution of Particulate

As mentioned in the previous subsection, data on particle size distribution for the 6V-71 bus engine were somewhat suspect due to an apparent leak in the sampling system. For this reason, the actual particle weights collected were meaningless; and therefore, only the percentages are tabulated and discussed. The percentage data are given in Table 40, and they show reasonable agreement throughout the size range. These sizing data are presented graphically in Figures 19 and 20, a log-probability plot and a semilog plot, respectively. Note that the dependent variable is "percent of particulate below ECD". The plots for these two sets of discs are very similar, and they compare quite well to corresponding data on the other two engines. It is concluded, therefore, that the sample line leak was upstream of the impactor and that the size distribution data are valid on a percentage basis.

TABLE 40. CRANKCASE PARTICULATE SIZING DATA FOR 6V-71 BUS ENGINE, 13-MODE COMPOSITE (STANDARD SPEEDS)

Impactor Stage Number	Minimum Diam.[a] Collected, microns	% Recovered by Set		Cumulative % by Set	
		109	113	109	113
filter	under 0.43	17.7	19.8	17.7	19.8
8	0.43	20.0	18.9	37.7	38.7
7	0.62	29.5	30.3	67.2	69.0
6	1.05	24.1	23.3	91.3	92.3
5	2.1	5.9	5.5	97.2	97.8
4	3.3	1.9	1.5	99.1	99.3
3	4.6	0.9	0.5	100.0	99.8
2	7.0	0.0	0.2	100.0	100.0
1	11.1	0.0	0.0	100.0	100.0

[a] "50 percent effective cutoff diameter" (ECD)

G. Amount and Boiling Point Distribution of Organic Solubles in Particulate

Total organic solubles in particulate were separated and determined by Soxhlet extraction, and boiling range was obtained via gas chromatograph. These properties are described in Table 41 along with boiling ranges on lubricating oils (new and used) for comparison. As an average, about 98 percent of the particulate matter was soluble. The solubles had slightly lower initial boiling points than new oil, while the used oil had a much higher IBP. Most of the remaining boiling ranges were quite similar, especially between

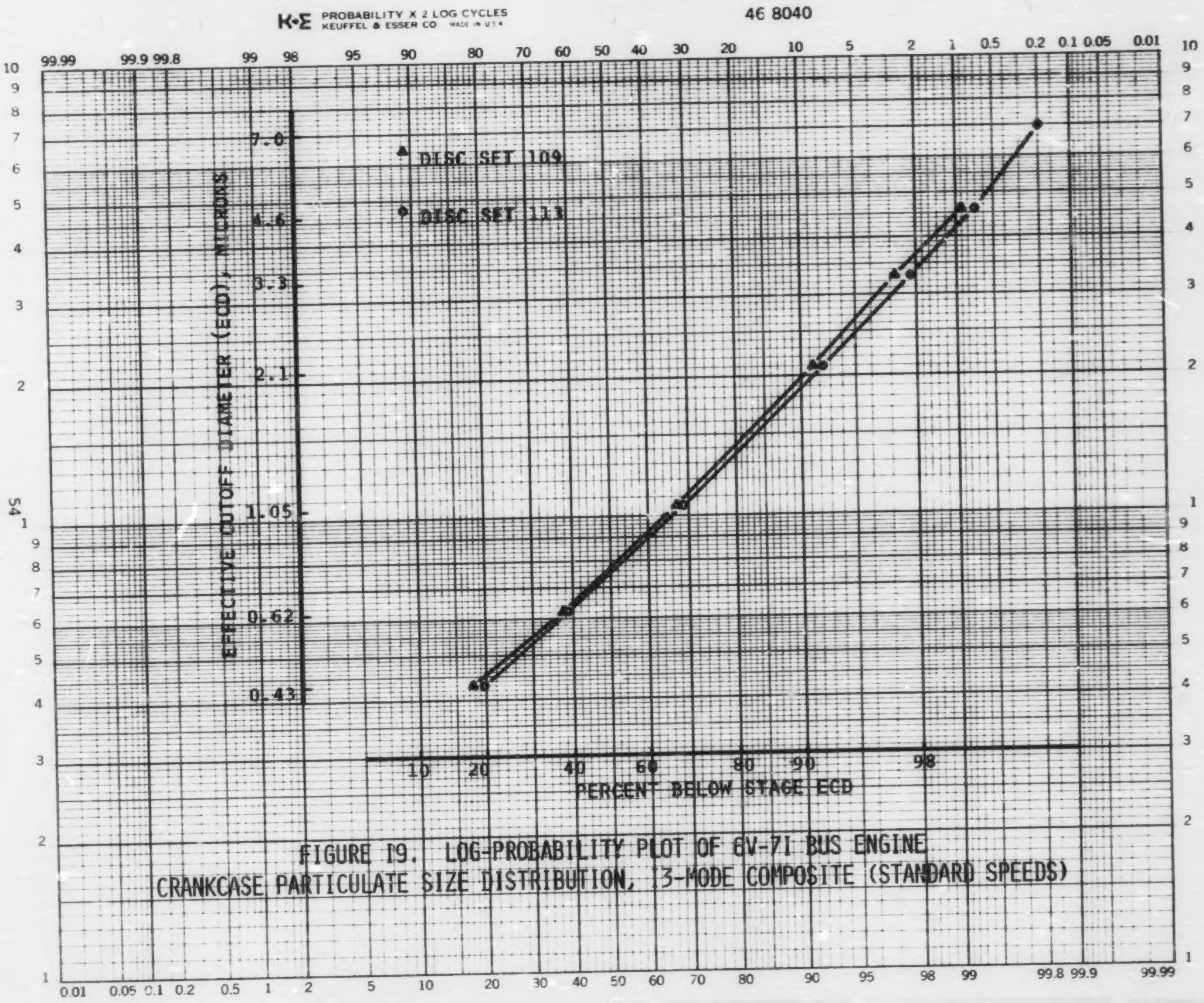

FIGURE 19. LOG-PROBABILITY PLOT OF 6V-71 BUS ENGINE CRANKCASE PARTICULATE SIZE DISTRIBUTION, 13-MODE COMPOSITE (STANDARD SPEEDS)

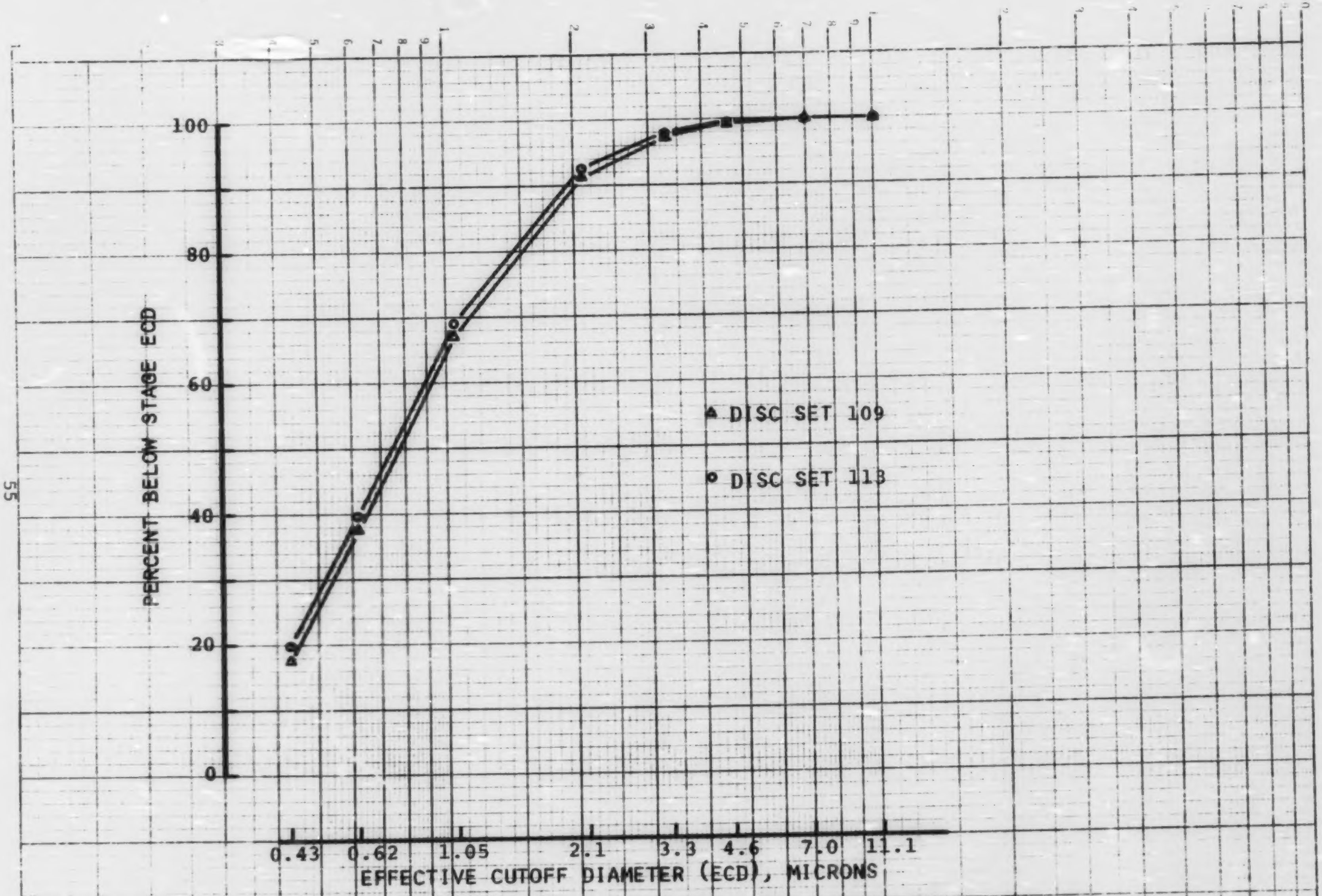

FIGURE 20. SEMILOG PLOT OF 6V-71 BUS ENGINE CRANKCASE PARTICULATE SIZE DISTRIBUTION, 13-MODE COMPOSITE (STANDARD SPEEDS)

40 and 90 percent points. It appears likely that this engine's crankcase particulate was mostly oil-derived, but that the particulate may have been more fuel-diluted than oil.

TABLE 41. AMOUNT AND BOILING RANGE OF SOLUBLES IN CRANKCASE PARTICULATE, 6V-71 BUS ENGINE, 13-MODE COMPOSITE (STANDARD SPEEDS)

Filter No.	Particulate, g	Solubles, g	% Solubles	Boiling Range of Solubles Temperature in °C at Weight % Off								
				1	10	20	40	60	80	90	95	97
AR-6025	1.541	1.510	98.0	264	415	457	477	499	528	565	619	--[a]
AR-6026	1.558	1.528	98.1	290	415	471	503	512	522	586	625	--[a]
AR-6027	1.573	1.543	98.1	293	420	477	506	524	551	585	---[a]	--[a]
Averages			98.1	282	417	468	495	512	534	579	622	--[a]
New oil for comparison				307	462	491	511	529	552	576	617	--[a]
Used oil for comparison				366	465	493	513	528	550	575	595	--[a]

[a] out of range of analysis

H. Benzo(α)Pyrene (BaP) in Particulate Organic Solubles

This polynuclear organic compound was measured as an indicator of total PNA in the soluble fraction of particulate. Data are given in Table 42 for the 6V-71 bus engine, expressed in several types of units. Emissions of BaP in crankcase particulate were computed on a mass rate (μg/hr) basis using the total sample collected as representative of a 39-minute period. BaP mass rate for this engine was higher than for either of the other two engines tested. Concentration of BaP in crankcase particulate was about the same for the two 6V-71 engines, but the bus engine's higher particulate emissions made its BaP mass emissions higher. Note that the BaP analysis method used probably resulted in high values as compared to newer methods.

TABLE 42. BaP CONTENT OF CRANKCASE PARTICULATE, 6V-71 BUS ENGINE, 13-MODE COMPOSITE (STANDARD SPEEDS)[a]

Filter No.	Total BaP, μg	Weight % BaP in Particulate	Weight % BaP in Solubles	BaP, μg/hr
AR-6025	40.3	0.0026	0.0027	61.6
AR-2027	60.2	0.0038	0.0039	92.0
Averages	50.2	0.0032	0.0033	76.8

[a] technique used produced high values as compared to newer methods

I. Elemental Composition of Particulate

Included in this subsection are data determined by combustion analysis at a commercial laboratory and X-ray data by the Institute's Mobile Energy Division. These data are given in Table 43, and they describe a predominantly hydrocarbon material with small amounts of other elements present. Hydrogen values for solubles (standard speeds).seem anomalously low, leading to a C/H ratio by weight of 7.09. The C/H ratio for solubles of particulate collected at low speeds is very similar to that for the engine's lubricating oil (6.57 versus 6.42). Data on particulate sulfur content by the two methods are in some disagreement. The X-ray data are considered to be more reliable.

TABLE 43. ELEMENTAL COMPOSITION OF CRANKCASE PARTICULATE, 6V-71 BUS ENGINE, 13-MODE COMPOSITE

Filter Nos.	Weight % of Particulate by Combustion				
	C	H	N	S	Σ CHNS
A47-6042 & 6043	86.8	11.7	0.7	0.7	99.9
A47-6044 & 6045	83.4	12.1	1.3	2.0	98.8
A47-6046 & 6047	78.7	11.3	1.3	0.9	92.2
Averages	83.0	11.7	1.1	1.2	97.0
A47-6052 & 6053[a]	82.4	12.6	0.2	1.7	96.9
A47-6054 & 6055[a]	84.4	12.8	0.1	0.6	97.9
Averages	83.4	12.7	0.2	1.2	97.4

Filter No.	Weight % of Particulate by X-ray			
	P	S	Cl	Zn
FH47-6044	0.06	0.25	---[b]	0.44
FH47-6046	0.07	0.26	---[b]	0.22
FH47-6048	0.09	0.27	0.01	---[b]
Averages	0.07	0.26	---[b]	0.22
FH47-6054[a]	0.08	0.21	0.01	0.28
FH47-6056[a]	0.07	0.22	0.03	0.41
Averages	0.08	0.22	0.02	0.34

[a] samples taken at low engine speeds (900 and 1500 rpm) - others at standard speeds

[b] none detected

J. Sulfate ($SO_4^=$) in Particulate

Sulfate in crankcase particulate was measured for the 6V-71 bus engine with results as shown in Table 44. These data show reasonable consistency, and it can be computed that the sulfur in the sulfate constituted about 18 percent of the X-ray sulfur at standard speeds and about 27 percent of the X-ray sulfur at low speeds. These figures are somewhat higher than for the other two engines.

TABLE 44. SULFATE IN CRANKCASE PARTICULATE, 6V-71 BUS ENGINE, 13-MODE COMPOSITE

Filter No.	μg $SO_4^=$ on Filter	S in $SO_4^=$ as Weight % Particulate	$SO_4^=$, mg/hr
FH47-6043	4.61	0.054	2.28
FH47-6045	3.82	0.040	1.92
FH47-6047	3.01	0.044	1.45
Averages	3.81	0.046	1.88
FH47-6053[a]	6.06	0.069	2.78
FH47-6055[a]	4.42	0.050	2.00
Averages	5.24	0.060	2.39

[a] samples taken at low engine speeds (900 and 1500 rpm) - others at standard speeds

VI. ANALYSIS FOR NITROSAMINES IN CRANKCASE GASES AND PARTICULATE

Part of the original test plan for this Task Order was sampling and analysis for nitrosamines in crankcase gases and particulate. This portion of the project has not yet been discussed, because the nitrosamine work was expanded beyond that called for in the original test plan. Due to this expansion and the importance of the nitrosamine studies to the project, all activity dealing with nitrosamines is collected in this section.

A. Summary of Project Efforts on Nitrosamines

The test plan for this project (Table 1) called for ten samples to be taken from each engine for nitrosamine analysis, five from crankcase gases and five from crankcase particulate. These samples were collected from the Detroit Diesel 6V-71 development engine, the Cummins NTC-350, and the Detroit Diesel 6V-71 bus engine. Collection and analysis systems will be described in Subsection VI.B.

The first additional nitrosamine activity was authorized under Task Change No. 1, dated October 4, 1976. Its purpose was to attempt confirmation of N-dimethylnitrosamine by GC-MS (Gas Chromatograph - Mass Spectrometer) in samples already obtained and analyzed as part of the original Task Scope of Work. Some samples were also taken for analysis by EPA and one of its other contractors, Research Triangle Institute.

Task Change No. 2, dated March 23, 1977, was added to collect one large sample and a number of smaller ones from a fourth engine and to analyze the samples by a variety of techniques. The engine employed was a Mack ETAY(B) 673-A which was being tested under another EPA Contract (No. 68-03-2417). Analyses were conducted by the Institute's Department of Environmental Sciences, EPA's Research Triangle Park laboratories, Research Triangle Institute, and EPA's National Enforcement Investigations Center in Denver.

B. Initial Sampling Systems

The system shown schematically in Figure 21 was used to collect gas samples for nitrosamine analysis, the collection medium being 25 ml of water in each impinger with a small amount of base (KOH) or a greater amount of buffer (Na_2CO_3) added to prevent the solution from becoming acidic. Like the two other impinger systems, it was designed to operate with a maximum flowrate of 4 liters per minute.

As reported by the Institute's Department of Environmental Sciences, the specific recovery of DMNA was determined by spiking a blank KOH solution with DMNA and subjecting it to the same procedures as the actual impinger sample. Blank glass fiber filters were similarly spiked and used for the recovery experiments. Quantitative determination of the DMNA was made by injecting 20 $\mu\ell$ of the sample extract into a gas chromatograph operated under the following conditions:

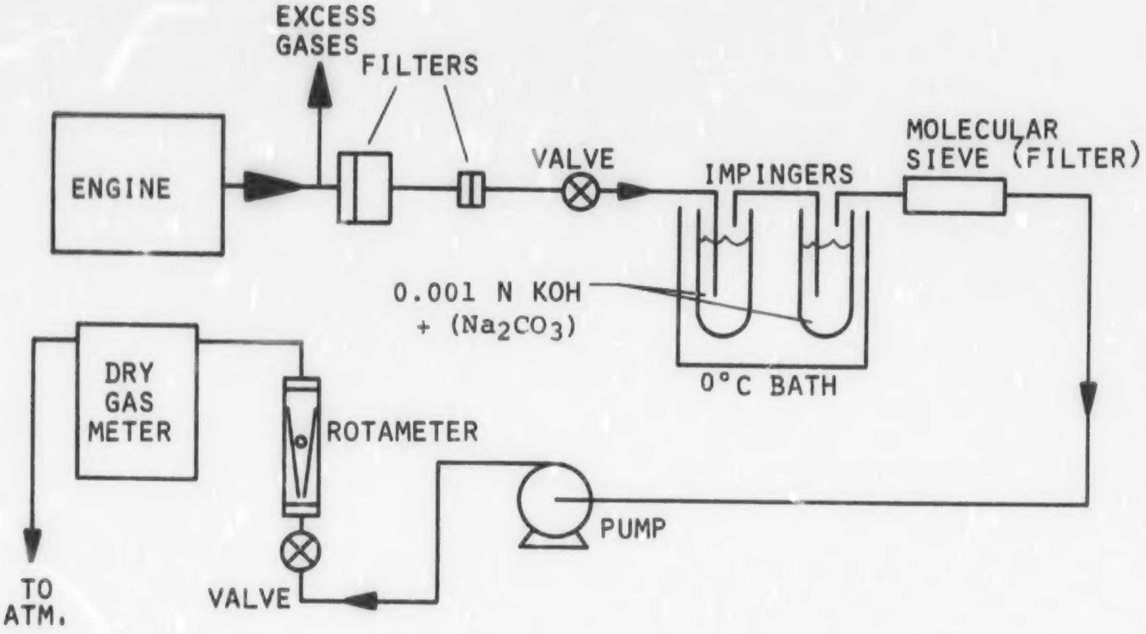
EXCESS GASES
FILTERS
ENGINE
VALVE
IMPINGERS
MOLECULAR SIEVE (FILTER)
0.001 N KOH + (Na_2CO_3)
0°C BATH
DRY GAS METER
ROTAMETER
PUMP
TO ATM.
VALVE

FIGURE 21. IMPINGER SYSTEM FOR COLLECTION OF CRANKCASE GAS SAMPLES FOR NITROSAMINE ANALYSIS

column:	0.9 m (ℓ) x 4 mm (i.d.) packed with Chromosorb 101 (80/100 mesh)
temperature:	inlet - 220°C column - 140°C transfer line - 210°C
detector:	Hall electrolytic conductivity, operated in the pyrolytic mode at 500°C, specific for nitrogen as ammonia.

Analysis for DMNA in crankcase particulate was conducted on samples collected by the hi-vol sampler on large glass fiber filters. The methodology used was essentially the same as that for gas samples, except that the samples were extracted from the filters in 0.01 normal KOH and distilled over into water. This water solution was then treated in the same way as the aqueous samples obtained in the impingers. More details of the analytical procedure are provided in the memoranda attached as pages C-2 and C-3 of Appendix C.

C. Analysis of Filter and Impinger Samples taken Under Initial Scope of Work

Data resulting from analysis of particulate samples taken during tests on the 6V-71 development engine, the NTC-350 engine, and the 6V-71 bus engine showed no evidence of nitrosamines. Likewise, no indication of nitrosamines was found in any of the impinger-collected engine intake air "blank" or "background" samples taken during these tests. A tabulation of the filters and impingers involved is included as Table C-1 of Appendix C, page C-4. Impinger-collected samples of crankcase gases, however, did show indications of N-dimethylnitrosamine using the Hall detector. It must be noted that these indications were not confirmed by GC-MS structural evidence. Subject to this qualification, data from impinger-collected gas samples are presented in Table 45 for the three engines mentioned above.

TABLE 45. CRANKCASE GAS DMNA RESULTS FOR 13-MODE COMPOSITE TESTS BY ENGINE, IMPINGER SAMPLES/HALL DETECTOR

Engine	Date	Impinger		DMNA[a], μg/m^3
		Run No.	Solution pH	
6V-71 Development	5/5/76	1	--[b]	0.58
	5/5/76	2	--[b]	0.99
	5/5/76	3	--[b]	0.27
	5/5/76	4	--[b]	0.54
	5/5/76	5	--[b]	0.58
	5/14/76	1	--[b]	0.45
NTC-350	7/13/76	1	6.3	0.95
	7/13/76	2	6.4	0.71
	7/13/76	3	7.2	0.24
	7/14/76	4	7.0	0.49
	7/14/76	5	7.2	0.42
	7/16/76	1	11.1[c]	0.56
	7/16/76	2	11.0[c]	0.39
6V-71 Bus	9/1/76	1	--[b,c]	0.10
	9/2/76	2	--[b,c]	0.085
	9/2/76	3	--[b,c]	0.085

[a] at p = 101.3 kPa and T = 21°C
[b] not determined
[c] contained Na_2CO_3 buffer

Although a base (0.001 N KOH) was used in all the impingers, it was determined while running the NTC-350 that some of the samples were turning slightly acidic toward the end of the sampling period. In order to avoid this situation, a buffer (Na_2CO_3) was added to subsequent impinger solutions to keep them basic. Comparing DMNA data for the first five samples from the NTC-350 to those for the last two, it appears that artifact formation in the unbuffered solutions was not a problem.

Concentrations of DMNA measured in gas samples from the first two engines are quite similar, on the average (0.57 $\mu g/m^3$ for the 6V-71 development engine versus 0.54 $\mu g/m^3$ for the NTC-350). Concentrations measured in gas samples from the 6V-71 bus engine are considerably lower, averaging 0.09 $\mu g/m^3$. No reasons are apparent which could account for this difference. It has been noted that the 6V-71 bus engine was operated on a No. 1 fuel, while the other engines were operated on a No. 2 fuel; but there is no evidence thus far to suggest that fuel type has any effect on measured concentrations of nitrosamines.

Using the data in Table 45 as basis, average volumetric concentrations and mass rates of DMNA measured in crankcase gases from the three engines are as follows: 0.17 ppb and 1.4 $\mu g/hr$ for the 6V-71 development engine; 0.15 ppb and 5.5 $\mu g/hr$ for the NTC-350; and 0.027 ppb and 0.35 $\mu g/hr$ for the 6V-71 bus engine. These data must be considered tentative until confirmed by reproducible structural evidence, which to date has not been obtained.

D. First Attempt at GC-MS Confirmation of DMNA

Prior to beginning work on this attempt at confirmation of the compound thought to be DMNA, the plan was to run the individual impinger-collected samples by GC-MS (12 samples remained from the earlier work). A problem arose, however, in that the highest liquid phase concentration which could be achieved with any of the individual samples was about 0.4 $ng/\mu\ell$. Sensitivity level of the GC-MS system was about 1.0 $ng/\mu\ell$ at best, with higher concentrations needed for better accuracy.

To provide a more concentrated sample for the GC-MS, it was decided to combine the existing samples and attempt to drive off the maximum amount of solvent at low temperature. Had no DMNA been lost in this procedure, its liquid phase concentration would have been about 2.2 $ng/\mu\ell$. Moderate losses (about 25 percent) were expected, but subsequent re-analysis by the Hall detector showed DMNA loss during concentration to be about 50 percent. There was no indication of DMNA in the combined sample when run on the GC-MS, so this test phase was inconclusive.

Samples were also taken during this same time period for dimethylamine analysis by EPA-RTP. Dimethylamine is considered to be a possible precursor of DMNA. Results of the evaluations indicated no dimethylamine in any of the samples taken. The same impinger-collection technique was used for these evaluations as was used for DMNA sample acquisition, except that the collection reagent was acidic (0.01 N H_2SO_4).

E. Collection and Analysis of Crankcase Gas Samples from Mack ETAY(B) 673-A Engine

Following the work described above on attempts to confirm the presence of DMNA by GC-MS, it was decided that another series of collection runs would be made in order to gather a larger sample. The previously-used engines were no longer on test stands or otherwise readily available, so the Mack ETAY(B) 673-A engine being used on another EPA contract was selected as a test engine. The experimental plan for this phase of the project was made up of these items:

- determine whether or not the Mack engine produces measurable amounts of DMNA in its crankcase gases, as analyzed by the impinger-collection/Hall detector method

- if the engine produces enough DMNA as characterized above, take a large sample of crankcase gases suitable for analysis by both Hall detector and GC-MS

- take small impinger samples, concurrent with large sample, for nitrosamine analysis by EPA-NEIC

- take small impinger samples (in acidic solution), concurrent with large sample, for amine (N-nitrosamine precursor) analysis by EPA-RTP

- take small Tenax-GC* trap samples, concurrent with large sample, for nitrosamine analysis by Research Triangle Institute

In order to simplify the sample acquisition process, it was decided to operate the engine at a steady-state condition of 1900 rpm and 25 percent load to gather the initial sample. This procedure permitted sampling at a constant rate and minimized engine fuel consumption. Fuel used was (code) EM-239-F, "National Average" No. 2 diesel fuel, the same batch as that used in the NTC-350 and 6V-71 development engines. Data on the initial sample (analysis by Hall detector) are summarized below:

sample rate (nominal)	4 liters/min (0.004 m^3/min)
gas sampled	0.108 std. m^3 (101.3 kPa & 21°C)
sample time	30.0 minutes
total DMNA recovered	16.2 ng
crankcase gas DMNA concentration	1.14 μg/std. m^3 (101.3 kPa & 21°C)

The DMNA standard analyzed at the same time as this sample shows only 13.2 percent recovery, whereas normal recoveries were 40 to 60 percent. This low apparent recovery contributed to the high (1.14 μg/m^3) calculated concentration of DMNA.

Based on these data, it was decided to collect 5000 ng of DMNA by using both a higher sample flowrate (with large impingers) and a longer sampling time. Using a projected sampling rate of 0.021 m^3/min (0.75 ft^3/min), time to acquire approximately 5000 ng of DMNA was calculated to be 26.5 hours.

The large-sample collection activity was performed on the Mack ETAY(B) 673-A engine, operating at 1900 rpm and 25 percent load. Fuel coded EM-239-F was used. Sampling was conducted over a period of three days, with impingers kept covered in an ice bath between (as well as during) sampling periods. The sampling hardware used was identical to that shown schematically in Figure 21, except that larger impingers were used in place of the midget impingers. Data on the large sample are summarized below, with analysis by Hall detector:

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* registered trademark of Enka N.V., The Netherlands

sample rate (nominal)	0.021 m^3/min (0.75 ft^3/min)
gas sampled	41.3 std. m^3 (101.3 kPa & 21°C)
sample time	30.0 hr
total DMNA recovered	2,380. ng
crankcase gas DMNA concentration	0.094 μg/std. m^3 (101.3 kPa & 21°C)

Although a substantial amount of DMNA was recovered from the large sample, it was only about half the target amount. Several factors may have combined to produce this result, including losses of DMNA during the three-day sampling period, recovery variation in the extraction and concentration steps, and variability in the engine's production of DMNA.

Having determined by the same methods used to analyze earlier samples that the compound identified as DMNA was present in sufficient quantity, attention was turned to GC-MS analysis of the large sample. The complete report filed by the Institute's Department of Environmental Sciences is included in Appendix C (pages C-5 through C-19) for reference. Summarizing their findings, standards containing both DMNA and N-diethylnitrosamine (DENA) were run by full-spectrum scanning and in the mass fragmentographic mode to determine GC-MS retention and response characteristics. The full-spectrum chromatogram of standards is shown in Figure 2a of the above-mentioned report, page C-11 of Appendix C. A single-ion scan at 74 amu is shown in Figure 2b (page C-12), indicating better resolution of the molecular ion of DMNA by computer regeneration. The mass fragment ion chromatograms of standards are shown in Figure 3 of the same report, page C-13 of Appendix C.

Chromatograms of diesel crankcase gas concentrate are shown in Figures 4 and 5 of the report by the Department of Environmental Sciences, pages C-14 through C-18 and page C-19 of Appendix C, respectively. The full-spectrum chromatogram in Figure 4a and the single-ion scans in Figures 4b through 4e are complicated by the presence of interfering compounds. This complication meant that it was not possible to extract "clean" spectra, but rather good indications of the presence of DMNA and DENA were obtained (at 30 and 74 amu for DMNA and at 30 and 102 amu for DENA). The mass fragmentograms of crankcase gas samples shown in Figure 5 can be compared to fragmentograms for standards in Figure 3 of the GC-MS report. The sample fragmentograms show strong evidence of the presence of DMNA and little visible evidence of the presence of DENA.

All the data and explanations thus far have dealt with impinger-collected gas samples from a diesel engine crankcase. The indications seem to be that nitrosamine compounds are present in such samples, whereas they are not present in impinger-collected samples of engine intake air or engine exhaust or in samples of particulate from diesel engine crankcases or exhausts. Test results to this point cannot, however, rule out the possibility that nitrosamines are formed as artifacts in the collection medium either during or after collection.

During each day of collection of the large sample, several smaller samples were acquired for independent analysis. The first such samples to be discussed are those sent to EPA's National Enforcement Investigations Center (NEIC) in Denver for nitrosamine analysis by gas chromatograph-thermal energy analyzer. Procedures for sample handling and analysis are detailed in EPA-

NEIC's report to the Project Officer and a copy of their nitrosamine analytical method, included as pages C-20 and C-21, respectively, of Appendix C. The samples were collected using the apparatus shown in Figure 21. Prior to shipment, the aqueous samples were treated in the following steps:

A. Quantitatively transfer the impinger solution to a 125 ml separatory funnel.

B. Add 13 g NaCl per 50 ml solution.

C. Extract with dichloromethane (3 x 10 ml), combine the extracts.

D. Place extract in light-tight glass bottles with Teflon* cap liners and pack carefully.

The results of the EPA-NEIC analysis have been combined with pertinent sampling data to yield the data shown in Table 46. These data confirm the presence of several nitrosamine compounds in the impinger-collected samples, as well as two other nitrogen-containing compounds. The amounts of DMNA measured in these samples (average 0.28 µg/m^3) fall between those found by the Department of Environmental Sciences in the original small sample from the ETAY(B)673-A engine (1.14 µg/m^3) and in the large sample subsequently analyzed by GC-MS (0.094 µg/m^3). The reasons for a lack of agreement are not known, but they may involve time lag between sampling and analysis as well as different collection/retention efficiencies for small (short-term) samples as compared to the large sample.

TABLE 46. SUMMARY OF EPA-NEIC NITROSAMINE ANALYSIS OF MACK ETAY(B)673-A CRANKCASE GAS SAMPLES

Date	Gas Sampled, std.[a] m^3	µg/std. m^3[a] by Compound[b]					
		DMNA	DENA	DBNA	NPIP	NMORPH	DANA
1/4/77	0.184	0.24	0.14	0.092	0.060	0.28	0.23
1/5/77	0.190	0.32	0.12	0.11	<DL	0.25	0.20
1/6/77	0.187	0.29	0.12	0.10	<DL	0.26	ND[c]
Detection Limits		0.027	0.027	0.059	0.043	0.053	0.13

[a] at 101.3 kPa and 21°C

[b] DMNA = N-dimethylnitrosamine
DENA = N-diethylnitrosamine
DBNA = N-dibutylnitrosamine
NPIP = N-nitrosopiperidine
NMORPH = N-nitrosomorphaline
DANA = N-diamylnitrosamine

[c] none detected

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* registered trademark of E. I. duPont DeNemours & Company

Another type of small sample was acquired during each day of large-sample collection, this one in an acidic impinger solution for nitrosamine precursor analysis. The particular constituent for which there was some reason to analyze was dimethylamine, since it was considered to be a possible precursor of the N-dimethylnitrosamine already tentatively identified in diesel crankcase gases. The samples sent to EPA's Research Triangle Park laboratories were analyzed by ion chromatography, and the only ions detectable were Na+, NH_4+, and K+ (as a shoulder on NH_4+ peak).

Qualification of these results should include a limitation on sensitivity of about 0.2 to 1 μg/ml in aqueous solution and the possibility that peaks representing methylamine and/or ethanolamine could be obscured by the ammonium and potassium peaks. The samples were not concentrated, so the sensitivity limits of the technique can be interpreted as follows:

Compound	Maximum Possible Undetected Crankcase Gas Concentration[a]
ethanolamine	300 μg/m^3
methylamine	300 μg/m^3
ethylamine	60 μg/m^3
dimethylamine	60 μg/m^3

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[a] at 101.3 kPa and 21°C

It can be seen that this initial ion chromatographic analysis was very coarse, since expected concentrations of amines would have been on the order of 1 μg/m^3. A letter report from EPA-RTP on this analysis and supporting ion chromatographic data are given in Appendix C, pages C-22 through C-27.

The third group of relatively small samples taken during the large-sample collection period was that taken on Tenax-GC cartridges for GC-MS analysis by Research Triangle Institute (RTI). Although sampling instructions were followed, analysis could not be conducted properly because the concentration of materials on the traps was too high. There was an initial indication thought to be DMNA on one of these over-loaded traps when it was examined by single-ion monitoring, but the compound was later discovered to be an interfering hydrocarbon (alkane or alkene) contaminant when a full mass spectrum was run. These traps had each sampled about 0.084 m^3 of filtered crankcase gases. Concern was also expressed by RTI that gases sampled onto the Tenax cartridges should not contain more than 5 ppm NO_x to insure against artifact formation.

Following the large-sample collection period, it was determined that the crankcase gas concentration of NO_x from the Mack ETAY(B)673-A was about 60 ppm at 1900 rpm and 25 percent load. It was agreed, therefore, that subsequent samples should be diluted by a (target) factor of 13.5. The resulting NO_x concentration would be about 4.4 ppm if the target dilution were achieved. The sample dilution and trapping process is explained in detail in SwRI's letter to RTI, included as pages C-28 through C-30 of Appendix C. In summary, it consisted of sampling a small amount of crankcase gas into a relatively large bag containing nitrogen, then mixing the gases and passing the total through a filter and a Tenax cartridge as before. Measurement of N_2

volume placed in the bag initially and of total gas removed from the bag yielded effective dilution ratio and amount of crankcase gas. Nominal 1 liter and 5 liter (0.001 m^3 and 0.005 m^3) samples of crankcase gas were taken and passed through traps.

Results of analysis on these dilute samples by RTI are given in its report to EPA, included as pages C-31 through C-43 of Appendix C. The single-ion mass chromatograms in Figures 2 and 3 of this report showed no DMNA, to detection limits of ∿166 ppt and ∿100 ppt, respectively. Translated into units consistent with other studies reported thus far, these upper limits on possible undetected DMNA were 0.51 and 0.31 $\mu g/m^3$, respectively. Note that all the DMNA results on impinger-collected samples from the Mack engine, from EPA-NEIC and from the Institute's Department of Environmental Sciences, are lower than these detection limits with the exception of the initial small sample by SwRI.

Analysis of another trap-collected sample (No. 6) was conducted by obtaining full mass spectra, producing identification of numerous organics as listed in Table 2 of the RTI report (page C-41). The compounds were not quantitated, but the major components as observed by the total ion current profile were phenol and N,N-dimethylacetamide. None of the compounds RTI considers N-nitrosamine precursors (dimethylamine, diethylamine, morpholine, etc.) were found, nor were any other amines detected. Detection limits for nitrosamines in this sample were about the same as those already discussed for sample No. 4.

Although not included in the RTI report due to time requirements, sample No. 5 was also subjected to a full scan. The (different) column used for this analysis gave better resolution of the sample as a whole, but it was not expected to yield good nitrosamine results. Data on this sample are given on pages C-44 through C-46. The N,N-dimethylacetamide was also a major constituent of this sample, as determined by the total ion current profile.

Finding the N,N-dimethylacetamide in the samples was not expected, and thus far no work has been done to determine its origin or possible further reactions. According to RTI, this compound has not been found in other emissions from internal combustion engines, but was found at trace levels in samples from a forest fire.

Reservations expressed by RTI about their results dealt mainly with the sampling procedure. One concern was the possibility that any DMNA present in the crankcase gas might have condensed on the walls of the sample bag. Another concern was that the sample lines were not heated, RTI having found earlier that line temperatures of about 50°C were required to minimize DMNA losses. Finally, the lack of a specific recovery experiment on an authentic standard created a certain lack of confidence in the overall results.

VII. DISCUSSION OF CRANKCASE EMISSION CONTROL POSSIBILITIES

A limited investigation has been made into possibilities for recirculation or other controls on diesel crankcase emissions, as called for in the Task Scope of Work. Due to the efforts required to complete other phases of the program, only a small effort could be devoted to this subject. No testing of crankcase emission control systems was performed.

In order to reduce oil emission from the crankcase, most engines employ baffles and low flow velocities in the breather passages. As evidenced by the results of this study, however, the oil control systems employed on the test engines were not adequate. It may be that most of the oil or oil-derived particles actually emitted were too small to be apprehended by passive mechanical control systems (baffles, etc.), and such systems could probably have at best a minor effect on gaseous crankcase emissions.

At least one retrofit system is currently being marketed (by CECA Engineering, Division of Kar Products) for crankcase emission control of stationary and marine diesels, but it does not appear to be usable on turbocharged or blown engines in its present state of development. The system is called "C.E.C.A." or "Clean Engine, Clear Air", and it operates by filtering crankcase gases and recirculating them to the inlet manifold. Such a system might be adapted to turbocharged or blown engines using a pump downstream of the filter and perhaps even a final charcoal filter element to trap hydrocarbon material. The information above was published on this system in Diesel and Gas Turbine Progress, April 1976.(7)

Some additional information on crankcase emission control systems used by five manufacturers of marine diesel engines was submitted for this report by the EPA Task Officer. This information on marine diesels, dated December 7, 1976, is summarized as follows:

Detroit Diesel-Allison Division, General Motors

The crankcase breather tube is routed to the air cleaner (or silencer) intake on all marine engines, turbocharged and naturally aspirated.

Electro-Motive Division, General Motors

The breather tube is connected to the exhaust system.

Cummins

Naturally aspirated - V903; internal breather connects to intake port
- all others; breather on valve cover connects to intake port

Turbocharged - VT903; breather tube connected to the air inlet
- all others; no control, vented to engine compartment

Deutz

Individual contacted was not directly involved with controls, but said that his opinion was that there were no controls (the breather tube is routed outside the engine compartment). Deutz is working on some systems in research.

Alco

No controls. The breather tube is routed out of the engine compartment.

Another manufacturer's viewpoint on crankcase emission controls for diesels is presented in the letter and report from Caterpillar Tractor Company presented as Appendix D. The Caterpillar viewpoint, in summary, is that diesel crankcase emissions are an insignificant air pollution source.

In this report section, we have primarily reported the work and opinions of others, since no testing of diesel crankcase emission control systems was conducted. It appears, however, that crankcase controls for naturally aspirated engines are feasible with available technology. Indeed, some such systems are in use; and data could be gathered on their performance in the field to determine whether they have positive or negative effects on engine performance and durability.

Adaptation of a recirculation system to a turbocharged engine is somewhat more complicated than adaptation of a system to a naturally aspirated engine, if it is considered necessary to add the blowby gases to the inlet tract downstream of the turbocharger. Such a system would require a pump to achieve flow in the desired direction. If the blowby gases were routed to the air cleaner, either directly or through some extra filter or trap system, no such pumping requirements would exist. Other alternatives might also be considered for some applications, such as directing crankcase gases into the engine's exhaust or simply cleansing them with filters plus hydrocarbon traps. Even in the case of turbocharged engines, therefore, crankcase emission control does not appear to be a difficult technical problem.

VIII. ANALYSIS OF TEST ENGINE LUBRICATING OILS

In addition to the demonstration and characterization data already presented, it was requested that information be obtained on the engine oils. These tests and measurements included the following:

infrared spectral analysis
quantitative metals by X-ray fluorescence
boiling range by ASTM D-2887
API gravity by ASTM D287
viscosity in centistokes at 100°F and 212°F by ASTM D445
pentane and benzene insolubles by ASTM D893
total acid number by ASTM D664
total base number by ASTM D2896
sulfated ash by ASTM D874
fuel dilution (of oil)
carbon, hydrogen, and nitrogen fractions by combustion.
benzo(α)pyrene

Boiling ranges have already been reported in conjunction with corresponding data on particulate solubles, so they will not be repeated here.

Copies of the infrared spectra of new and used oils for all four engines are given in Appendix E, and their interpretations are given here. Spectra 900 and 901 (pages E-2 and E-3) are for the 6V-71 development engine, and they show that the used oil is essentially unchanged from new oil. Oxidation of the used oil is negligible, and no water or ethylene glycol is present. Some soot is present in the used oil, and both contain a poly-isobutylene type viscosity index improver.

Spectra 902 and 903 (pages E-4 and E-5) show differences in new and used oils for the NTC-350 engine. The oil's additive package is partially consumed in the used oil, and there are slight traces of oxidation and nitration. The additive package mentioned includes sulfonates (detergents and dispersants) and zinc (ZDDP) anti-oxidants and anti-scuffing agents. Soot is present in the used oil, and its viscosity index improver (poly methyl methacrylate type) is intact. No ethylene glycol or water is present in either new or used oil.

Spectra 930 and 931 (pages E-6 and E-7) are for the 6V-71 bus engine's oils, and there are differences in new and used oils. Soot appears in the used oil, and the additive package in the used oil is partially consumed. The used oil's viscosity index improver is intact (same type as in NTC-350 oils), and no water or ethylene glycol is present in either sample. In general, both used oils from the characterization engines show changes in properties which are normal for oils after considerable service.

Spectra 1166 and 1167 (pages E-8 and E-9) are for the Mack ETAY(B)673-A oils. Very little soot appears in the used oil, and no water or ethylene glycol are present in either new or used oil. Part of the zinc additive package in the used oil has decomposed, as it is designed to do with use. A small amount of oxidation has taken place in the used oil, and its (poly methyl methacrylate type) viscosity index improver is intact.

The remaining data on lubricating oils can be summarized in tabular form, and Table 47 provides this information. Most of these data show little difference between new and used oils, and the oils from the four engines are also quite similar to one another in most respects. Differences which are noticeable, however, show up in sulfur concentrations between engines. Viscosity at 100°F is also considerably lower for the ETAY(B)673-A oil than for the others. Used oils seem more viscous excepting that from the 6V-71 development engine, and acid numbers of used oils were higher except for the 6V-71 bus oil. Small amounts of fuel dilution were observed for all the used oils except that from the 6V-71 development engine. BaP values were quite scattered, and are probably higher than those which would have been determined by newer analytical techniques.

TABLE 47. DATA ON PROPERTIES OF NEW AND USED LUBRICATING OILS FROM THE FOUR TEST ENGINES

Engine	6V-71 Development		NTC-350		6V-71 bus		ETAY(B)673-A	
Oil Description	Texaco URSA Super 3, SAE 30		Chevron Delo 400, SAE 30, Mil. L2104C		Gulf SAE 40, Mil. 46152		Shell Rotella T, SAE 15W - 40, Mil. 50012	
Oil History	New	Used	New	Used	New	Used	New	Used
X-ray data, wt. %								
Phosphorus (P)	0.11	0.12	0.10	0.12	0.12	0.11	0.13	0.14
Sulfur (S)	0.65	0.69	0.51	0.51	0.34	0.28	0.35	0.39
Chlorine (Cl)	------[a]	------[a]	0.023	0.027	------[a]	------[a]	0.01	0.01
Iron (Fe)	------[a]	0.004	------[a]	0.001	------[a]	0.005	------[a]	0.007
Zinc (Zn)	0.10	0.10	0.10	0.10	0.15	0.13	1.23	1.26
Calcium (Ca)	0.20	0.21	0.28	0.26	0.21	0.19	0.25	0.27
Combustion data, wt. %								
Carbon (C)		86.9	86.3	86.3	86.3	86.0	84.4	84.2
Hydrogen (H)		13.1	13.4	13.3	13.6	13.4	12.8	13.0
Nitrogen (N)		0.04	0.03	0.02	0.02	0.03	0.12	0.12
API gravity, °API @ 60°F	26.9	26.8	27.2	27.4	27.7	27.5	28.3	27.7
Density, g/ml @ 60°F	0.893	0.894	0.892	0.891	0.889	0.890	0.886	0.889
Viscosity, cs @ 100°F	129.6	127.6	121.7	133.7	152.5	156.5	109.4	119.6
Viscosity, cs @ 212°F	12.3	12.3	12.5	13.4	14.6	14.9	14.5	15.0
Pentane insolubles, wt. %	0.017	0.017	0.013	0.057	0.035	0.041	0.15	0.18
Benzene insolubles, wt. %	0.012	0.000	0.000	0.047	0.034	0.041	0.09	0.04
Total acid number[c]	1.66	2.18	3.21	3.92	2.82	2.60	3.21	3.78
Total base number[d]	5.83	5.55	5.55	4.71	5.04	5.04	8.51	7.39
Sulfated ash, wt. %	0.79	0.81	1.05	0.99	0.81	0.75	1.01	1.07
Fuel dilution, wt. %[e]	------[b]	0.0	------[b]	0.4	------[b]	0.7	------[b]	<0.4
BaP, μg/g oil[f]	no data	33.	no data	39.	16.	19.	7.6	23.

[a] none detected
[b] not measured
[c] expressed in mg KOH/gram sample
[d] expressed as 1.159 (mg $HClO_4$/gram sample)
[e] portion of oil sample boiling between n-C_{12} and n-C_{20} paraffins
[f] probably higher than results which would have been obtained by newer methods

REFERENCES

1. Hare, Charles T., "Methodology for Determining Fuel Effects on Diesel Particulate Emissions." Final Report No. EPA-650/2-75-056 to the U.S. Environmental Protection Agency under Contract No. 68-02-1230, March 1975.

2. Chevalier, C. E., "Hydrocarbon Content of the Blowby Gases of Severely Worn Automotive Diesel Engines." Report No. 15 prepared under Contract No. PHS 86-64-76 with the U. S. Department of Health, Education, and Welfare, October 1964.

3. Federal Register, Vol. 37, No. 221, Part II, Subparts H and J (November 15, 1972).

4. Stump, Fred, "Oxygenated Compounds in Automobile Exhaust - Gas Chromatographic Procedure." Unpublished Procedure developed by the U.S. Environmental Protection Agency.

5. Black, F. M.; High, L. E.; and Sigsby, J. E.; "Methodology for Assignment of a Hydrocarbon Photochemical Reactivity Index for Emissions from Mobile Sources." Final Report No. EPA-650/2-75-025 to the U.S. Environmental Protection Agency, March 1975.

6. Tejada, Silvestre, "Determination of Soluble Sulfates." Unpublished Procedure developed by the U.S. Environmental Protection Agency, 1974.

7. Diesel and Gas Turbine Progress, Vol. XLII, No. 4, April 1976.

APPENDIX A

TASK ORDER 4 SCOPE OF WORK AND MODIFICATIONS

SCOPE OF WORK

TASK I

Southwest Research Institute (SwRI) shall adapt the appropriate measurement procedures and methodology for sampling and analyzing gases and particulates in diesel engine blowby emissions. The following compounds will be analyzed for:

Gaseous form:

a) Total hydrocarbons
b) Light hydrocarbons - individual analysis of C_1 through nC_4
c) CO and CO_2
d) NO_x
e) O_2
f) Aldehydes - Total polar aldehydes and individual aldehydes through C_6. C_3's will be analyzed as a group.
g) Nitrosamines

Particulate:

a) Total particulate
b) Distribution of particulate size. This shall be performed with an Anderson impactor. Some of the impactor plates shall be analyzed by a scanning electron microscope to determine the size distribution of the impacted particules.
c) Nitrosamines
d) Total organic solubles
e) C,H,N, and S (particulate)
f) Boiling range of solubles
g) Sulfate
h) BaP in solubles

SwRI shall also evaluate diesel blowby in terms of potential emissions of significant quantities of other compounds that could represent environmental or health hazards. Should such compounds be judged a potential emission product, SwRI shall report said compounds to the Project Officer. This evaluation will be based on contractor knowledge and experience in addition to the contractor's analysis of the results of the above tests. For example, if the contractor finds significant levels of BaP, he might report that significant levels of other POM compounds could be present in the blowby. This is because BaP is only one POM and is the one used to characterize the POM content of the stream being analyzed. If significant levels of BaP were to be found, this could indicate significant levels of the other POM's.

TASK II

SwRI shall employ the sampling and analysis methodology adapted in Task I to characterize the blowby emissions of two engines. One of the engines will be a heavy duty truck type 4-stroke and the other a city bus type 2-stroke. SwRI shall acquire the engines from local fleet sources. Both engines will be characteristic of the heavy duty engines of their class that are currently in use. Both engines shall have accumulated sufficient hours of use to have reached about the half way point between being a new engine and one that is in need of a major rebuilding. These hours of use shall be over roughly that type of use expected of the engine type.

The engines shall be tested with lubricating oil that has accumulated approximately one half of the use that the manufacturer recommends. The fuel to be used shall be Number 1 Diesel fuel for the 2-stroke and Number 2 Diesel fuel for the 4-stroke. Both fuels shall approximate the national average composition for fuels of their type. The test cycle shall be the 13-mode cycle or some variant thereof which closely resembles the 13-mode cycles. Final choice of the 13-mode cycle will be dependent on sample size and tire cooling problems, and will be made by mutual agreement between SwRI and the Project Officer.

TASK III

SwRI shall examine the possibilities for blowby recirculation or other techniques for the control of diesel blowby emissions. The results of this analysis shall be included in the final report. This analysis shall consist of a brief paper study that employs the contractor's knowledge and experience in addition to his contacts with technical people from the engine manufacturers. If the contractor feels that this study is promising, he shall do some limited engine experimentation such as installing a PCV system and checking engine emissions.

Reports and Time Requirements

The technical effort involved in performing this Scope of Work should require six months to perform. During this time, SwRI shall submit monthly letter reports briefly summarizing the status of the work and the resource expenditures. Three weeks after the end of this Period of Performance SwRI shall submit to the Task Officer five (5) copies of the draft final report. Two weeks after receipt of this report the Project Officer shall return the approved report to SwRI for final editing and reproduction. Three weeks after SwRI receives the reviewed draft final report, SwRI shall submit to the Task Officer 50 copies of the final report.

CONTRACT TASK SPECIFICATION CHANGE REQUEST NEGOTIATED CONTRACTS BRANCH CONTRACTS MANAGEMENT DIVISION ENVIRONMENTAL PROTECTION AGENCY NATIONAL ENVIRONMENTAL RESEARCH CENTER CINCINNATI, OHIO 45268 11-4291	EPA CONTRACT NO. 68-03-2196 CONTRACTOR Southwest Res. Institute TASK NO. 04 TASK CHANGE NO. 1
TASK (short descriptive title) Diesel Crankcase Emissions Characterization	DATE 8-24-76

ACCOUNTING AND APPROPRIATION DATA

Appropriation	DCN	Contract No.	Acct. No.	OC	Amt.	SFO

TASK SPECIFICATIONS OR DESCRIPTION

Add the following Task IV to the Scope of Work:

The contractor shall perform, or have performed, gas chromatographic-mass spectroscopic (GC-MS) analyses for N-Dimethylnitrosamine (DMNA) on samples obtained from the crankcase blowby generated by the heavy duty diesel engines tested in this Task Order. The samples subjected to the GC-MS analysis should be taken from runs that have produced samples that have responded positively to the DMNA analysis system. About twelve samples should be analyzed by the GC-MS

In addition to the breakdown of costs required in the contract billing instructions, vouchers/invoices must also identify the allocation of costs to each Task Order.

ESTIMATE OF	GOVERNMENT ESTIMATE	CONTRACTOR ESTIMATE
Task Level of Effort	160 hours	same
DURATION OF TASK	One additional month	same
TASK COMPLETION DATE	September 28, 1976	

	ORG. CODE	TELEPHONE	DATE
Merrill W. Korth PROJECT OFFICER - Merrill W. Korth			

APPROVALS (as applicable)	SIGNATURE	DATE
CONTRACTOR	Southwest Research Institute	
TITLE	R. E. Chatten, Asst. Mgr., Contract Administration	9/29/76
SIGNATURE	Original Signed by R. E. Chatten	
CONTRACTING OFFICER	/s/ Albert H. Allquist	10/4/76

CONTRACT TASK SPECIFICATION CHANGE REQUEST

NEGOTIATED CONTRACTS BRANCH
CONTRACTS MANAGEMENT DIVISION
ENVIRONMENTAL PROTECTION AGENCY
NATIONAL ENVIRONMENTAL RESEARCH CENTER
CINCINNATI, OHIO 45268

EPA CONTRACT NO 68-03-2196 11-4291

CONTRACTOR Southwest Research Institute

TASK NO. ~~II~~ 4

TASK CHANGE NO. 2

DATE

TASK (Short descriptive title) "Diesel Crankcase DMNA Emissions"

ACCOUNTING AND APPROPRIATION DATA

Appropriation	DCN	Contract No.	Acct. No.	OC	Amt.	SFO

TASK SPECIFICATIONS OR DESCRIPTION

As per Scope of Work

In addition to the breakdown of costs required in the contract billing instructions, vouchers/invoices must also identify the allocation of costs to each Task Order.

ESTIMATE OF	GOVERNMENT ESTIMATE	CONTRACTOR ESTIMATE
Task Level of Effort	$5,000 210 hours	
DURATION OF TASK	2 months after initiation	
TASK COMPLETION DATE	2 months after initiation	

	ORG. CODE	TELEPHONE	DATE
Merrill W Korth PROJECT OFFICER - Merrill W. Korth, ECTD			

APPROVALS (as applicable)	SIGNATURE	DATE
CONTRACTOR	Southwest Research Institute	
TITLE	S. H. Birgel, Manager Contract Administration	March 21, 1977
SIGNATURE	Original signed by S. H. Birgel	
CONTRACTING OFFICER	/s/ Albert H. Ahlquist	3/23/77

Scope of Work

Task I Engine Selection

Southwest Research Institute (SwRI) shall sample the crankcase blowby emissions of the Mack ETAY(B) 673(A) diesel engine that is being used in EPA Contract No. 68-03-2417 to establish whether or not sufficient N-dimethylnitrosamine (DMNA) is being emitted to provide a sample capable of being analyzed by the SwRI gas chromatograph - mass spectrometer (GC-MS). The following decision line will then be pursed:

a. If insufficient DMNA flow is found - In this case, SwRI will perform the same test on other diesel engines that are currently on test stands. If one is found that emits sufficient sample, proceed to Task II. If not, then the DDAD 6V-71 sampling methodology development engine that was used in Task Order 04 of this contract shall be mounted on the test stand, followed by the effort described in Task II.

b. If sufficient DMNA is found, proceed with Task II.

Task II Sample Acquisition

The engine selected in Task I shall be operated over the appropriate modes and the following samples drawn:

1. Sufficient sample for the SwRI GC-HEC and GC-MS systems to analyze.

2. Samples drawn through cartridges supplied by ORD/MSERC, to be returned to them for analysis.

3. Samples drawn in SwRI impengers, extracted and sent to EPA/NEIC, Denver.

Task III Sample Analysis

SwRI shall analyze the samples drawn in Task II, by the GC-HEC and GC-MS techniques.

APPENDIX B

GASEOUS EXHAUST EMISSIONS DATA ON THREE DIESEL ENGINES

TABLE B-1. 13-MODE FEDERAL DIESEL EXHAUST EMISSION CYCLE
6V-71 DEVELOPMENT ENGINE, TEST 1

Mode	Engine Speed rpm	Torque lb-ft	Power bhp	Fuel Flow lb/min	Air Flow lb/min	Exhaust Flow lb/min	Fuel -Air Ratio
1	440	3.5	0.3	0.04	12.19	12.23	0.003
2	1260	10.5	2.5	0.13	24.54	24.67	0.005
3	1260	134.8	32.3	0.27	29.08	29.35	0.009
4	1260	271.4	65.1	0.45	30.09	30.54	0.015
5	1260	406.2	97.4	0.63	30.19	30.82	0.021
6	1260	542.7	130.2	0.92	30.83	31.76	0.030
7	440	5.3	0.4	0.05	15.54	15.59	0.003
8	2100	479.7	191.8	1.33	49.80	51.14	0.027
9	2100	358.9	143.5	1.04	53.65	54.70	0.019
10	2100	239.8	95.9	0.77	53.21	53.99	0.015
11	2100	119.0	47.6	0.54	51.27	51.80	0.010
12	2100	8.8	3.5	0.31	47.87	48.18	0.007
13	440	3.5	0.3	0.05	9.93	9.98	0.005

Mode	HC ppm	CO ppm	CO_2 %	NO** ppm	Weighted bhp	BSHC g/hp hr	BSCO* g/hp hr	$BSCO_2$ g/hp hr	$BSNO_2$** g/hp hr	Hum. gr/lb
1	97	110	0.81	96	0.02					72.6
2	158	218	1.07	54	0.20					72.6
3	81	151	2.06	175	2.59	0.97	3.62	773	6.84	72.6
4	86	108	3.31	337	5.21	0.53	1.33	641	6.82	72.6
5	108	155	4.75	669	7.80	0.45	1.29	621	9.15	72.6
6	104	4148	6.52	879	10.42	0.33	26.61	657	9.26	72.6
7	98	124	0.82	91	0.03					76.0
8	136	652	6.39	992	15.34	0.48	4.57	704	11.42	76.0
9	94	92	5.00	627	11.48	0.47	0.92	787	10.33	76.0
10	72	50	3.71	361	7.67	0.54	0.73	863	8.77	76.0
11	70	63	2.56	163	3.81	1.01	1.79	1151	7.66	76.0
12	118	127	1.51	59	0.28					76.0
13	137	96	0.81	88	0.02					74.3

Cycle Composite BSHC = 0.720 gram/bhp hr
BSCO* = 6.604 gram/bhp hr
$BSNO_2$** = 9.800 gram/bhp hr
BSHC + $BSNO_2$** = 10.521 gram/bhp hr
$BSCO_2$ = 801. gram/bhp hr
BSFC = 0.483 lb/bhp hr

* converted to wet basis

** converted to wet basis, corrected to 75 grains of water per lb of dry air and corrected to 85°F inlet temperature per Federal Register para. 85.974-18

TABLE B-2. 13-MODE FEDERAL DIESEL EXHAUST EMISSION CYCLE 6V-71 DEVELOPMENT ENGINE, TEST 1

Mode	Engine Speed rpm	Torque lb-ft	Power bhp	Fuel Flow lb/min	Air Flow lb/min	Exhaust Flow lb/min	Fuel -Air Ratio
1	440	1.8	0.1	0.04	13.07	13.12	0.003
2	1260	10.5	2.5	0.13	28.06	28.19	0.005
3	1260	134.8	32.3	0.28	29.91	30.19	0.009
4	1260	271.4	65.1	0.45	30.01	30.46	0.015
5	1260	406.2	97.4	0.64	30.65	31.29	0.021
6	1260	542.7	130.2	0.92	32.68	33.60	0.028
7	400	1.8	0.1	0.04	14.71	14.75	0.003
8	2100	479.7	191.8	1.33	51.62	52.96	0.026
9	2100	358.9	143.5	1.03	51.79	52.82	0.020
10	2100	239.8	95.9	0.78	54.46	55.24	0.014
11	2100	119.0	47.6	0.53	53.14	53.67	0.010
12	2100	8.8	3.5	0.32	50.07	50.39	0.006
13	440	1.8	0.1	0.05	11.58	11.63	0.004

Mode	HC ppm	CO ppm	CO_2 %	NO** ppm	Weighted bhp	BSHC g/hp hr	BSCO* g/hp hr	$BSCO_2$ g/hp hr	$BSNO_2$** g/hp hr	Hum. gr/lb
1	81	89	0.82	101	0.01					79.3
2	122	173	1.08	55	0.20					79.3
3	80	119	2.14	188	2.59	0.99	2.91	826	7.58	79.3
4	74	62	3.43	364	5.21	0.46	0.76	663	7.36	79.3
5	96	131	4.81	711	7.80	0.41	1.10	638	9.86	79.3
6	106	3839	6.56	958	10.42	0.36	26.06	699	10.68	79.3
7	94	120	0.82	102	0.01					77.6
8	136	627	6.34	1047	15.34	0.50	4.55	723	12.49	77.6
9	96	99	4.93	671	11.48	0.47	0.96	749	10.68	77.6
10	75	62	3.73	374	7.67	0.57	0.94	887	9.32	77.6
11	72	83	2.55	174	3.81	1.07	2.45	1187	8.48	77.6
12	94	132	1.53	64	0.28					77.6
13	117	109	0.81	100	0.01					77.7

Cycle Composite BSHC = 0.699 gram/bhp hr
BSCO* = 6.489 gram/bhp hr
$BSNO_2$** = 10.677 gram/bhp hr
BSHC + $BSNO_2$** = 11.375 gram/bhp hr
$BSCO_2$ = 822. gram/bhp hr
BSFC = 0.482 lb/bhp hr

* converted to wet basis

** converted to wet basis, corrected to 75 grains of water per lb of dry air and corrected to 85°F inlet temperature per Federal Register para. 85.974-18

TABLE B-3. 13-MODE FEDERAL DIESEL EXHAUST EMISSION CYCLE OF TRUCK WITH CUMMINS NTC-350 ENGINE, TEST 1 (3 min/mode)

Mode	Engine Speed rpm	Torque lb-ft	Power bhp	Fuel Flow lb/min	Air Flow lb/min	Exhaust Flow lb/min	Fuel -Air Ratio
1	600	0.0	0.0	0.07	7.89	7.96	0.009
2	1500	20.3	5.8	0.24	18.09	18.33	0.013
3	1500	252.1	72.0	0.53	21.43	21.97	0.025
4	1500	507.7	145.0	0.92	23.34	24.25	0.039
5	1500	759.8	217.0	1.27	25.53	26.79	0.050
6	1500	1015.4	290.0	1.82	32.54	34.36	0.056
7	600	0.0	0.0	0.07	8.29	8.36	0.008
8	2100	885.3	354.0	2.28	52.61	54.89	0.043
9	2100	662.8	265.0	1.75	44.24	45.99	0.040
10	2100	442.7	177.0	1.23	36.93	38.16	0.033
11	2100	220.1	88.0	0.72	28.44	29.16	0.025
12	2100	17.5	7.0	0.52	25.10	25.63	0.021
13	600	0.0	0.0	0.07	8.29	8.35	0.008

Mode	HC ppm	CO* ppm	CO_2 %	NO** ppm	Weighted bhp	BSHC g/hp hr	BSCO* g/hp hr	$BSCO_2$ g/hp hr	$BSNO_2$** g/hp hr	Hum., gr/lb
1	134	189	1.77	145	0.00					92.2
2	86	186	2.84	184	0.46					92.2
3	67	234	5.41	430	5.76	0.27	1.88	682	5.67	92.2
4	48	648	8.68	1113	11.60	0.11	2.85	600	8.04	92.2
5	39	1761	10.89	1770	17.36	0.06	5.72	555	9.44	92.2
6	36	2466	12.30	2045	23.20	0.06	7.68	602	10.47	96.4
7	124	140	1.69	133	0.00					96.4
8	37	1099	9.55	1419	28.32	0.08	4.48	612	9.51	96.4
9	27	754	8.70	1116	21.20	0.06	3.44	624	8.37	96.4
10	22	448	7.28	686	14.16	0.06	2.54	648	6.39	96.4
11	14	289	5.43	392	7.04	0.06	2.52	743	5.61	96.4
12	22	271	4.36	278	0.56					96.4
13	72	188	1.70	126	0.00					96.4

Cycle Composite BSHC = 0.113 gram/bhp hr
BSCO* = 4.659 gram/bhp hr
$BSNO_2$** = 8.910 gram/bhp hr
BSHC + $BSNO_2$** = 9.023 gram/bhp hr
$BSCO_2$ = 663 gram/bhp hr

* converted to wet basis

** converted to wet basis and corrected to 75 grains water per lb dry air

TABLE B-4. 13-MODE FEDERAL DIESEL EXHAUST EMISSION CYCLE OF TRUCK WITH CUMMINS NTC-350 ENGINE, TEST 2 (3 min/mode)

Mode	Engine Speed rpm	Torque lb-ft	Power bhp	Fuel Flow lb/min	Air Flow lb/min	Exhaust Flow lb/min	Fuel -Air Ratio
1	600	0.0	0.0	0.07	7.80	7.87	0.009
2	1500	20.3	5.8	0.25	18.59	18.84	0.013
3	1500	252.1	72.0	0.53	19.71	20.24	0.027
4	1500	507.7	145.0	0.92	23.71	24.63	0.039
5	1500	759.8	217.0	1.27	26.11	27.38	0.049
6	1500	1015.4	290.0	1.82	32.05	33.87	0.057
7	600	0.0	0.0	0.06	6.81	6.87	0.009
8	2100	885.3	354.0	2.28	53.55	55.84	0.043
9	2100	662.8	265.0	1.75	44.98	46.73	0.039
10	2100	442.7	177.0	1.23	36.59	37.83	0.034
11	2100	220.1	88.0	0.72	27.84	28.56	0.026
12	2100	17.5	7.0	0.45	25.52	25.97	0.018
13	600	0.0	0.0	0.07	7.99	8.06	0.009

Mode	HC ppm	CO* ppm	CO_2 %	NO** ppm	Weighted bhp	BSHC g/hp hr	BSCO* g/hp hr	$BSCO_2$ g/hp hr	$BSNO_2$** g/hp hr	Hum., gr/lb
1	118	137	1.80	133	0.00					108.7
2	90	160	2.87	186	0.46					108.7
3	54	260	5.89	497	5.76	0.20	1.92	684	6.04	108.7
4	31	672	8.57	1067	11.60	0.07	3.00	601	7.83	108.7
5	10	1557	10.80	1841	17.36	0.02	5.17	563	10.03	108.7
6	1	2340	12.55	2046	23.20	0.00	7.19	605	10.32	99.1
7	100	146	1.80	152	0.00					99.1
8	41	996	9.38	1415	28.32	0.09	4.13	611	9.64	99.1
9	33	644	8.57	1137	21.20	0.08	2.99	624	8.66	99.1
10	37	416	7.38	694	14.16	0.10	2.34	651	6.41	99.1
11	32	288	5.56	419	7.04	0.14	2.46	745	5.87	100.8
12	68	248	3.76	257	0.56					100.8
13	106	167	1.76	138	0.00					100.8

Cycle Composite BSHC = 0.113 gram/bhp hr
BSCO* = 4.312 gram/bhp hr
$BSNO_2$** = 9.041 gram/bhp hr
BSHC + $BSNO_2$** = 9.154 gram/bhp hr
$BSCO_2$ = 662 gram/bhp hr

* converted to wet basis
** converted to wet basis and corrected to 75 grains water per lb dry air

TABLE B-5. 13-MODE FEDERAL DIESEL EXHAUST EMISSION CYCLE OF TRUCK WITH CUMMINS NTC-350 ENGINE, TEST 3 (3 min/mode)

Mode	Engine Speed rpm	Torque lb-ft	Power bhp	Fuel Flow lb/min	Air Flow lb/min	Exhaust Flow lb/min	Fuel -Air Ratio
1	600	0.0	0.0	0.07	7.78	7.85	0.009
2	1500	20.3	5.8	0.26	19.57	19.83	0.013
3	1500	252.1	72.0	0.53	19.37	19.91	0.027
4	1500	507.7	145.0	0.92	24.55	25.47	0.037
5	1500	759.8	217.0	1.28	26.26	27.54	0.049
6	1500	1015.4	290.0	1.82	35.20	37.02	0.052
7	600	0.0	0.0	0.07	7.92	7.98	0.009
8	2100	885.3	354.0	2.28	53.32	55.60	0.043
9	2100	662.8	265.0	1.75	44.73	46.48	0.039
10	2100	442.7	177.0	1.23	35.88	37.11	0.034
11	2100	220.1	88.0	0.72	28.59	29.31	0.025
12	2100	17.5	7.0	0.45	25.41	25.86	0.018
13	600	0.0	0.0	0.07	8.21	8.28	0.009

Mode	HC ppm	CO* ppm	CO_2 %	NO** ppm	Weighted bhp	BSHC g/hp hr	BSCO* g/hp hr	$BSCO_2$ g/hp hr	$BSNO_2$** g/hp hr	Hum., gr/lb
1	112	184	1.80	131	0.00					92.2
2	81	211	2.80	188	0.46					92.2
3	44	293	5.95	522	5.76	0.16	2.13	680	6.24	92.2
4	30	565	8.30	992	11.60	0.07	2.61	602	7.53	92.2
5	13	1684	10.89	1820	17.36	0.02	5.62	571	9.98	92.2
6	1	2587	12.85	2120	23.20	0.00	8.69	677	11.69	98.1
7	101	183	1.78	154	0.00					98.1
8	47	901	9.42	1411	28.32	0.10	3.72	611	9.57	98.1
9	44	614	8.59	1072	21.20	0.10	2.83	622	8.12	98.1
10	35	451	7.51	741	14.16	0.10	2.49	650	6.71	98.1
11	54	133	5.41	399	7.04	0.24	1.17	744	5.74	98.1
12	79	299	3.77	266	0.56					96.4
13	125	208	1.70	155	0.00					96.4

Cycle Composite BSHC = 0.127 gram/bhp hr
BSCO* = 4.502 gram/bhp hr
$BSNO_2$** = 9.202 gram/bhp hr
BSHC + $BSNO_2$** = 9.329 gram/bhp hr
$BSCO_2$ = 676 gram/bhp hr

* converted to wet basis
** converted to wet basis and corrected to 75 grains water per lb dry air

TABLE B-6. 13-MODE FEDERAL DIESEL EXHAUST EMISSION CYCLE
OF DETROIT DIESEL 6V-71 BUS ENGINE, TEST 1 HIGH SPEED (3 min/mode)

Mode	Engine Speed rpm	Torque lb-ft	Power bhp	Fuel Flow lb/min	Air Flow lb/min	Exhaust Flow lb/min	Fuel -Air Ratio
1	515	0.0	0.0	0.05	11.79	11.84	0.004
2	1260	12.3	2.9	0.17	30.96	31.12	0.005
3	1260	119.0	28.6	0.25	30.11	30.36	0.008
4	1260	238.1	57.1	0.44	30.21	30.65	0.015
5	1260	357.1	85.7	0.61	30.39	31.01	0.020
6	1260	476.2	114.2	0.89	30.21	31.10	0.030
7	515	0.0	0.0	0.06	11.77	11.83	0.005
8	2100	388.6	155.4	1.30	48.70	50.00	0.027
9	2100	290.6	116.2	1.00	48.38	49.38	0.021
10	2100	194.3	77.7	0.77	49.28	50.05	0.016
11	2100	96.3	38.5	0.54	48.54	49.08	0.011
12	2100	8.8	3.5	0.37	49.12	49.48	0.007
13	515	0.0	0.0	0.05	11.66	11.71	0.004

Mode	HC ppm	CO* ppm	CO_2 %	NO** ppm	Weighted bhp	BSHC g/hp hr	BSCO* g/hp hr	$BSCO_2$ g/hp hr	$BSNO_2$** g/hp hr	Hum. gr/lb
1	1024	861	0.71	39	0.00					77.7
2	915	752	1.07	67	0.24					77.7
3	464	328	2.06	325	2.28	6.51	9.18	903	14.92	77.7
4	572	133	3.21	658	4.57	4.05	1.87	712	15.24	77.7
5	460	158	4.51	928	6.85	2.20	1.51	674	14.51	77.7
6	504	4107	6.21	897	9.14	1.81	29.41	698	10.55	71.1
7	780	724	0.65	47	0.00					71.1
8	380	1127	5.99	973	12.43	1.61	9.53	796	13.52	71.1
9	288	125	4.71	825	9.30	1.62	1.40	827	15.14	71.1
10	308	73	3.65	559	6.22	2.62	1.24	971	15.54	68.1
11	432	103	2.45	353	3.08	7.27	3.45	1290	19.43	68.1
12	416	227	1.61	178	0.28					68.1
13	872	568	0.66	68	0.00					68.1

Cycle Composite BSHC = 4.017 gram/bhp hr
BSCO* = 10.595 gram/bhp hr
$BSNO_2$** = 14.852 gram/bhp hr
BSHC + $BSNO_2$** = 18.869 gram/bhp hr
$BSCO_2$ = 888. gram/bhp hr

* converted to wet basis
** converted to wet basis and corrected to 75 grains water per lb dry air

TABLE B-7. 13-MODE FEDERAL DIESEL EXHAUST EMISSION CYCLE OF DETROIT DIESEL 6V-71 BUS ENGINE, TEST 2 HIGH SPEED (3 min/mode)

Mode	Engine Speed rpm	Torque lb-ft	Power bhp	Fuel Flow lb/min	Air Flow lb/min	Exhaust Flow lb/min	Fuel -Air Ratio
1	515	0.0	0.0	0.05	11.69	11.74	0.004
2	1260	14.0	3.4	0.16	31.05	31.21	0.005
3	1260	119.0	28.6	0.28	30.22	30.50	0.009
4	1260	239.8	57.5	0.45	30.87	31.31	0.014
5	1260	358.9	86.1	0.64	30.03	30.66	0.021
6	1260	479.7	115.1	0.87	29.74	30.62	0.029
7	515	0.0	0.0	0.06	11.59	11.65	0.005
8	2100	392.1	156.8	1.31	48.23	49.54	0.027
9	2100	294.1	117.6	1.00	48.23	49.23	0.021
10	2100	196.1	78.4	0.77	48.23	49.00	0.016
11	2100	98.0	39.2	0.56	48.23	48.79	0.012
12	2100	14.0	5.6	0.38	49.28	49.66	0.008
13	515	0.0	0.0	0.06	11.76	11.82	0.005

Mode	HC ppm	CO* ppm	CO_2 %	NO** ppm	Weighted bhp	BSHC g/hp hr	BSCO* g/hp hr	$BSCO_2$ g/hp hr	$BSNO_2$** g/hp hr	Hum. gr/lb
1	936	754	0.68	55	0.00					66.4
2	941	843	1.07	67	0.27					66.4
3	458	340	2.06	321	2.28	6.46	9.55	907	14.79	66.4
4	520	137	3.22	674	4.60	3.74	1.96	724	15.84	66.4
5	476	184	4.56	923	6.89	2.24	1.72	671	14.20	66.4
6	580	4477	6.20	852	9.21	2.04	31.33	681	9.79	63.0
7	792	601	0.66	59	0.00					63.0
8	416	1311	6.02	958	12.54	1.73	10.89	786	13.07	63.0
9	268	128	4.68	850	9.41	1.48	1.40	809	15.38	63.0
10	352	89	3.32	583	6.27	2.90	1.47	857	15.75	75.9
11	440	112	2.34	371	3.14	7.23	3.68	1203	19.96	75.9
12	416	237	1.68	190	0.45					75.9
13	800	615	0.64	56	0.00					75.9

Cycle Composite BSHC = 4.028 gram/bhp hr
BSCO* = 11.307 gram/bhp hr
$BSNO_2$** = 14.717 gram/bhp hr
BSHC + $BSNO_2$** = 18.744 gram/bhp hr
$BSCO_2$ = 861. gram/bhp hr

* converted to wet basis

** converted to wet basis and corrected to 75 grains water per lb dry air

TABLE B-8. 13-MODE FEDERAL DIESEL EXHAUST EMISSION CYCLE OF DETROIT DIESEL 6V-71 BUS ENGINE, TEST 1 LOW SPEED (3 min/mode)

Mode	Engine Speed rpm	Torque lb-ft	Power bhp	Fuel Flow lb/min	Air Flow lb/min	Exhaust Flow lb/min	Fuel -Air Ratio
1	515	0.0	0.0	0.04	11.70	11.74	0.003
2	900	12.3	2.1	0.11	22.75	22.86	0.005
3	900	124.3	21.3	0.20	22.29	22.49	0.009
4	900	248.6	42.6	0.34	22.92	23.26	0.015
5	900	372.9	63.9	0.48	23.26	23.74	0.021
6	900	498.9	85.5	0.69	22.40	23.09	0.031
7	515	0.0	0.0	0.05	11.50	11.55	0.004
8	1500	467.4	133.5	1.01	35.42	36.43	0.029
9	1500	348.4	99.5	0.75	35.49	36.24	0.021
10	1500	232.8	66.5	0.54	35.95	36.48	0.015
11	1500	115.5	33.0	0.37	35.55	35.92	0.010
12	1500	8.8	2.5	0.20	36.31	36.52	0.006
13	515	0.0	0.0	0.05	11.69	11.74	0.004

Mode	HC ppm	CO* ppm	CO_2 %	NO** ppm	Weighted bhp	BSHC g/hp hr	BSCO* g/hp hr	$BSCO_2$ g/hp hr	$BSNO_2$** g/hp hr	Hum. gr/lb
1	1096	558	0.75	68	0.00					69.7
2	1016	864	0.92	60	0.17					69.7
3	797	349	1.99	339	1.70	11.11	9.69	868	15.45	69.7
4	444	178	3.26	680	3.41	3.20	2.56	735	16.05	69.7
5	516	336	4.65	929	5.11	2.53	3.28	713	14.31	69.7
6	668	8266	5.96	837	6.84	2.38	58.71	665	9.77	69.7
7	960	617	0.69	69	0.00					69.4
8	396	2277	6.12	1030	10.68	1.43	16.34	690	12.14	69.4
9	312	122	4.32	915	7.96	1.50	1.17	650	14.40	69.4
10	358	109	2.95	659	5.32	2.59	1.57	668	15.62	69.4
11	346	215	1.94	343	2.64	4.97	6.15	872	16.11	72.6
12	578	667	1.09	67	0.20					72.6
13	880	703	0.68	66	0.00					75.8

Cycle Composite BSHC = 4.322 gram/bhp hr
BSCO* = 17.793 gram/bhp hr
$BSNO_2$** = 13.943 gram/bhp hr
BSHC + $BSNO_2$** = 18.265 gram/bhp hr
$BSCO_2$ = 756. gram/bhp hr

* converted to wet basis
** converted to wet basis and corrected to 75 grains water per lb dry air

TABLE B-9. 13-MODE FEDERAL DIESEL EXHAUST EMISSION CYCLE OF DETROIT DIESEL 6V-71 BUS ENGINE, TEST 2 LOW SPEED (3 min/mode)

Mode	Engine Speed rpm	Torque lb-ft	Power bhp	Fuel Flow lb/min	Air Flow lb/min	Exhaust Flow lb/min	Fuel -Air Ratio
1	515	0.0	0.0	0.05	11.69	11.74	0.004
2	900	10.5	1.8	0.10	23.38	23.48	0.004
3	900	124.3	21.3	0.19	22.60	22.79	0.009
4	900	250.3	42.9	0.31	22.60	22.91	0.014
5	900	374.6	64.2	0.47	22.60	23.07	0.021
6	900	500.7	85.8	0.70	22.69	23.39	0.031
7	515	0.0	0.0	0.05	11.67	11.72	0.004
8	1500	465.7	133.0	1.02	35.72	36.74	0.029
9	1500	348.4	99.5	0.75	35.91	36.66	0.021
10	1500	232.8	66.5	0.54	36.16	36.70	0.015
11	1500	115.5	33.0	0.37	35.79	36.16	0.010
12	1500	10.5	3.0	0.21	35.72	35.93	0.006
13	515	0.0	0.0	0.06	11.77	11.82	0.005

Mode	HC ppm	CO* ppm	CO_2 %	NO** ppm	Weighted bhp	BSHC g/hp hr	BSCO* g/hp hr	$BSCO_2$ g/hp hr	$BSNO_2$** g/hp hr	Hum. gr/lb
1	835	728	0.74	64	0.00					74.2
2	984	824	0.91	61	0.14					74.2
3	780	372	1.97	352	1.70	11.02	10.47	871	16.27	74.2
4	452	145	3.20	721	3.43	3.19	2.04	706	16.64	74.2
5	544	276	4.57	1018	5.14	2.58	2.61	678	15.80	74.2
6	732	8260	6.04	875	6.86	2.63	59.22	680	10.30	74.2
7	1016	502	0.65	56	0.00					70.9
8	440	2126	6.33	1033	10.64	1.60	15.44	722	12.33	70.9
9	364	88	4.56	973	7.96	1.77	0.85	694	15.49	70.9
10	400	70	3.24	635	5.32	2.91	1.01	738	15.13	70.9
11	386	213	2.06	345	2.64	5.58	6.14	932	16.33	69.4
12	612	639	1.13	86	0.24					69.4
13	756	647	0.65	58	0.00					69.4

Cycle Composite BSHC = 4.473 gram/bhp hr
BSCO* = 17.361 gram/bhp hr
$BSNO_2$** = 14.440 gram/bhp hr
BSHC + $BSNO_2$** = 18.913 gram/bhp hr
$BSCO_2$ = 780. gram/bhp hr

* converted to wet basis
** converted to wet basis and corrected to 75 grains water per lb dry air

APPENDIX C

SUPPLEMENTAL NITROSAMINE DATA AND ANALYSIS REPORTS

Memorandum

May 27, 1976

To: Daniel Montalvo - Division 11

From: Charles F. Rodriguez - Division 01

Subject: Determination of nitrosamine in diesel blowby.
Project 11-4291-006

We have completed analyses of the impinger solutions and glass fiber filters which you used to sample diesel blowby exhaust. The methods we found that best extract dimethylnitrosamine (DMNA) from the sample medium follow.

I. Extraction from glass fiber filters

A. Cut the filter into small pieces and place in a 200 ml round bottom flask,

B. Add 75 ml 0.01 N KOH solution to the flask,

C. Distill approximately 45 ml into a 100 ml beaker containing 5 ml H_2O,

D. Wash the distillation tube with a small volume deionized water into the beaker,

F. Proceed as below, steps A - E.

II. Extraction from alkaline impinger solution

A. Quantitatively transfer the impinger solution to a 125 ml separatory funnel,

B. Add 10 ml hexane and shake for 1 minute, withdraw and discard the hexane,

C. Extract with dichloromethane (2 x 10 ml), combine the extracts,

D. Evaporate the extract to less than 500 µl with a Kuderna-Danish evaporative concentrator,

E. Make up the extract to a final volume of 500 µl with dichloromethane.

Memorandum

October 20, 1976

To: Charles Hare - 11

From: Charles F. Rodriguez - 01

Subject: Method for the determination of Dimethylnitrosamine in diesel blowby 11-4291-006

I am sending you a copy of the method we have used to extract samples taken from diesel blowby gases and determine the dimethylnitrosamine levels. The method is essentially the same except after step II. B-NaCl is added to the impinger solution in the amount of 13g per 100 ml solution. This serves to enhance the partition ratio of the DMNA in our favor and provides a better phase separation between the aqueous and organic liquids.

CFR: nn
File: 11-4291-006

TABLE C-1. SUPPLEMENTARY DATA ON CRANKCASE PARTICULATE AND ENGINE INTAKE AIR SAMPLES ANALYZED FOR NITROSAMINES

Engine	Date	Impinger		Filter No.
		Run No.	Solution pH	
6V-71 Development	3/23/76	-----[a]	-----[a]	AR-6001
	4/22/76	-----[a]	-----[a]	AR-6007
	4/26/76	-----[a]	-----[a]	AR-6008
	4/26/76	-----[a]	-----[a]	AR-6010
	4/26/76	-----[a]	-----[a]	AR-6011
	5/14/76	1	-----[b]	-------[a]
NTC-350	7/06/76	-----[a]	-----[a]	AR-6012
	7/06/76	-----[a]	-----[a]	AR-6013
	7/07/76	-----[a]	-----[a]	AR-6014
	7/07/76	-----[a]	-----[a]	AR-6015
	7/07/76	-----[a]	-----[a]	AR-6016
	7/13/76	3	8.7	-------[a]
	7/16/76	2	11.0	-------[a]
6V-71 Bus	8/25/76	-----[a]	-----[a]	AR-6028
	8/25/76	-----[a]	-----[a]	AR-6029
	8/25/76	-----[a]	-----[a]	AR-6030
	9/01/76	1	-----[b]	-------[a]

[a] does not apply

[b] not measured

SWRI DEPARTMENT OF ENVIRONMENTAL SCIENCES

CONFIRMATION OF THE PRESENCE OF DIMETHYLNITROSAMINE IN DIESEL BLOWBY GASES

GAS CHROMATOGRAPHY/MASS SPECTROMETRY

For some time now we have been quantitatively determining one nitrogen-containing compound in diesel crankcase gas samples and reporting it as n-dimethylnitrosamine. This compound is among those sampled in aqueous KOH and subsequently removed by extraction into dichloromethane, back extracted with acid to remove interfering amines, and concentrated by evaporation in a micro Kuderna-Danish apparatus. Quantitative determination of the compound called n-dimethylnitrosamine is then done by injection onto a gas chromatographic column which separates compounds of a similar nature. They are then sensed by a Hall Electrolytic Conductivity Detector operated in the pyrolytic mode (which makes it selective for amines and nitrosamines)(1,2). Regardless of the specificity of this detector, there is no molecular information provided. Consequently, identification of n-dimethylnitrosamine cannot be considered absolute. This program then was initiated to attempt confirmation of the identity of the compound heretofore called n-dimethylnitrosamine.

EXPERIMENTAL

Quantitative Determination of DMNA

The sample which was received dissolved in approximately 500 ml 0.01N KOH was transferred to a large separatory funnel, and NaCL (26 g/100 ml) was added. Extraction of amines, nitrosamines, and any other basic compounds was effected with three 50 ml volumes of dichloromethane (DCM). The combined extracts were transferred to a Kuderna-Danish evaporative concentrator and placed in a water bath maintained at 58-60°C. Volume was reduced, by evaporation of the DCM, to less than 5 ml. The concentrate was then made up to 5 ml with DCM and back extracted with mild H_2SO_4 solution to remove free amines. A quantitative determination was made by comparing chromatographic response of an aliquot with those of standard solutions of DMNA which had been subjected to the same extraction and concentration procedures. The extract was then transferred to a micro-Kuderna-Danish concentrator, 0.25 ml methanol was added, and the solution was evaporated to a final volume of approximately 300 µl. Methanol was then added to make the final concentration of DMNA 10 ng/µl as determined by the quantitative results above.

Quantitative determinations were made with a Model 220 gas chromatograph equipped with a Hall electrolytic conductivity detector operated in the pyrolytic mode. The instrument was operated under the following conditions:

Column: 0.9 m(l) x 4 mm (i.d.) packed with Chromosorb 101
(80/100 mesh)

Carrier Gas: Helium, 60 cc/min @ 50 psig

Temperature: Inlet - 220°C
Column - 140°C
Transfer line - 210°C

Detector: Quartz tube reaction zone
Inert helium atmosphere
Furnace - 500°C

Gas chromatographic/mass spectrometric determinations were made with a Finnigan Model 3300F instrument and Model 6100 data system operated under the following conditions:

Column: 1.5 m(l) x 2 mm (i.d.) packed with Chromosorb 101
(80/100 mesh)

Carrier Gas: Helium, 15 cc/min @ 14 psig

Temperature: Inlet - 220°C
Column - 150° - 250°C @ 6°/min
Glass Jet separator - 220°C
Column effluent transfer - 200°C
Separator transfer - 200°C
Ion Source: 70°-80°C

Mass Spectrometer
Electron impact ionization
Ionizing voltage - 70 ev @ 250 μ amp
Accelerating voltage - programmable, set for optimum resolution and sensitivity
Mass range: 29-105 amu
Integration time: 11 msec/amu
Scan Time: 1 sec

Results and Discussion

Gas chromatography with the Hall detector-equipped instrument indicated there was a total of 2380 ng in the concentrated blowby extract. The smallest volume we felt the extract could be concentrated to was 350 μl, which provided a concentration of 6.8 ng/μl DMNA. The chromatogram of 20 μl extract (136 ng DMNA) is shown here as Figure 1. Two peaks are shown as coinciding with the retention times of n-dimethylnitrosamine (DMNA) and n-diethylnitrosamine (DENA). These are the only two peaks normally observed when smaller samples of blowby exhaust were taken. In several of those samples, only the peak labeled DMNA was seen.

There are at least four and possibly six other compounds shown here which respond as nitrosamines, although it is by no means certain that they are not some other type of nitrogen-containing compounds.

Once it was determined that there was a workable amount of DMNA in the extract, GC-MS studies were begun by determining retention and response characteristics of authentic standards of DMNA and DENA. The mass spectrometer was set to scan in either the continuous, full spectrum mode or the mass fragmentographic mode at 30, 42, 74 and 102 amu. The chromatogram produced by full-spectrum scanning is shown as Figure 2, and that for the mass fragmentographic mode as Figure 3.

The chromatogram in Figure 2 is 1 ng of each compound, and it is apparent that at this level the nitrosamines are barely discernible. Thus for the full-spectrum mode the limit of detection is approximately 10 ng. Figure 2 shows, however, that an identifiable chromatogram can be extracted with the computer by having it regenerate the chromatogram of response at 74 amu only, the molecular ion of DMNA.

The mass spectra and the fragment ions that give rise to these spectra have been described(3,4). The use of these characteristic fragment ions to provide useful chromatographic data is shown in Figure 3. There is a response at 30, 42, and 74 amu for DMNA; and at 30, 42, and 102 amu for DENA. There is a difference noted in the relative abundances of these fragments when compared with those in the literature (which indicate the molecular ion is the most abundant). Here the ion at 42 amu is the most abundant. This situation is not uncommon and arises from differences in instruments and operating conditions. The operating conditions for chromatographing the blowby concentrate were established by running these standards, and were used throughout this study.

The full-spectrum (total ion) chromatogram of the diesel blowby concentrate is shown in Figure 4a. It is apparent that there is a large number of compounds in the extract, many more than had been expected. This complication made the situation much more difficult. The single-ion responses at 30, 42, 74 and 102 amu were computer-extracted from this chromatogram, and are shown as Figures 4b - 4e, respectively. The response at 42 amu has to be ignored because it saturates at an early point in the chromatogram. The combination of responses at 30 and 74 amu for DMNA, and at 30 and 102 amu for DENA indicate the presence of these compounds. It was not possible, however, to extract a "clean" spectrum from either of these regions of the chromatogram.

A mass fragmentogram was recorded for the diesel blowby concentrate and is shown in Figure 5. The response shown for DMNA very clearly indicates the presence of the three characteristic fragment ions at 30, 42, and 74 amu. They also occurred in the expected order of abundance, i.e., 42 amu the most abundant and 30 amu the least abundant. The presence of DENA is also indicated, but in a much less definitive fashion due to the overlapping of peaks at 42 amu. The oscilloscope output monitored by the GC-MS operator showed a definite peak indicating DENA at 102 amu, but the computer calculates on a relative response basis and plots from these results. Therefore, the presence of a large peak at 42 amu tended to make the plotted peak at 102 amu difficult to see.

The evidence presented here is a very strong indication that the compound previously reported as dimethylnitrosamine in diesel blowby concentrates is in fact that compound. To make identification of DMNA absolute, it would be required to isolate the DMNA from interfering compounds and thereby be able to produce a "clean" mass spectrum of DMNA. The identification of DENA in the concentrate is less clear-cut, as pointed out previously, due to the smaller amount present. Nevertheless, there is some evidence to support the identification of this compound as DENA. The problem of determining the origin of these species; i.e., "Are the nitrosamines produced in the diesel crankcase system or are they artifacts of sampling and/or analysis?", was not addressed here because it was beyond the scope of this project.

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1. "Gas Chromatography and Selective Detection of N-nitrosamines." J. W. Rhoades and D. E. Johnson, J. Chromato. Sci., 8, 616 (1970)

2. "Method for the Determination of N-nitrosamines in Tobacco-Smoke Condensate." J. W. Rhoades and D. E. Johnson, J. Natl. Cancer Inst., 48, 1841 (1972)

3. "Mass Spectrometry of Pesticides and Pollutants." S. Safe and O. Hutzinger, CRC Press, 1973 p. 204

4. "N-nitrosodimethylamine in Fish Meal." N. P. Sen, L. A. Schwinghamer, B. A. Donaldson and W. F. Miles, J. Agr. Food Chem., 20, 1280 (1972)

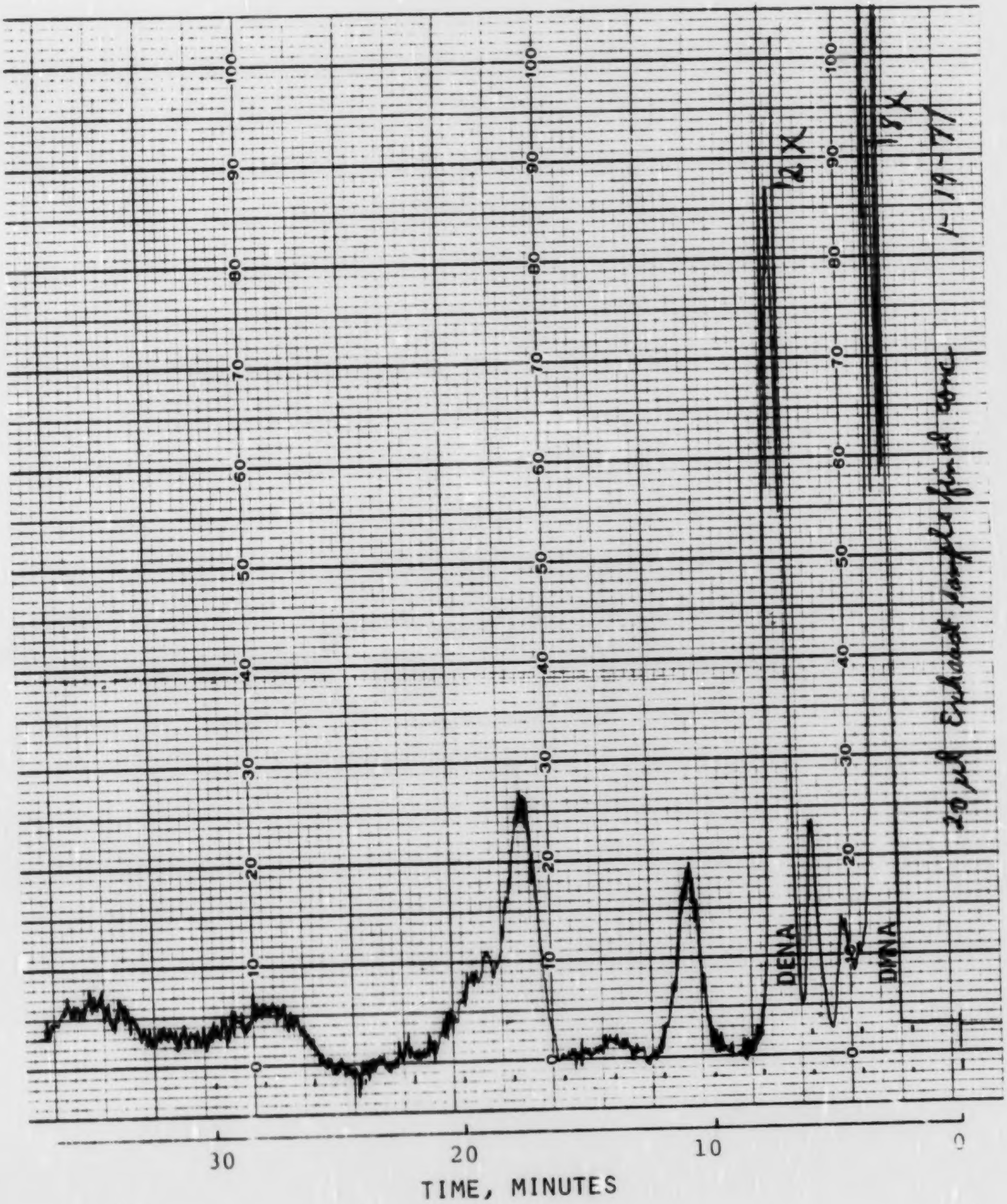


FIGURE C-I. CHROMATOGRAM OF BLOWBY EXHAUST, HALL NITROGEN DETECTOR

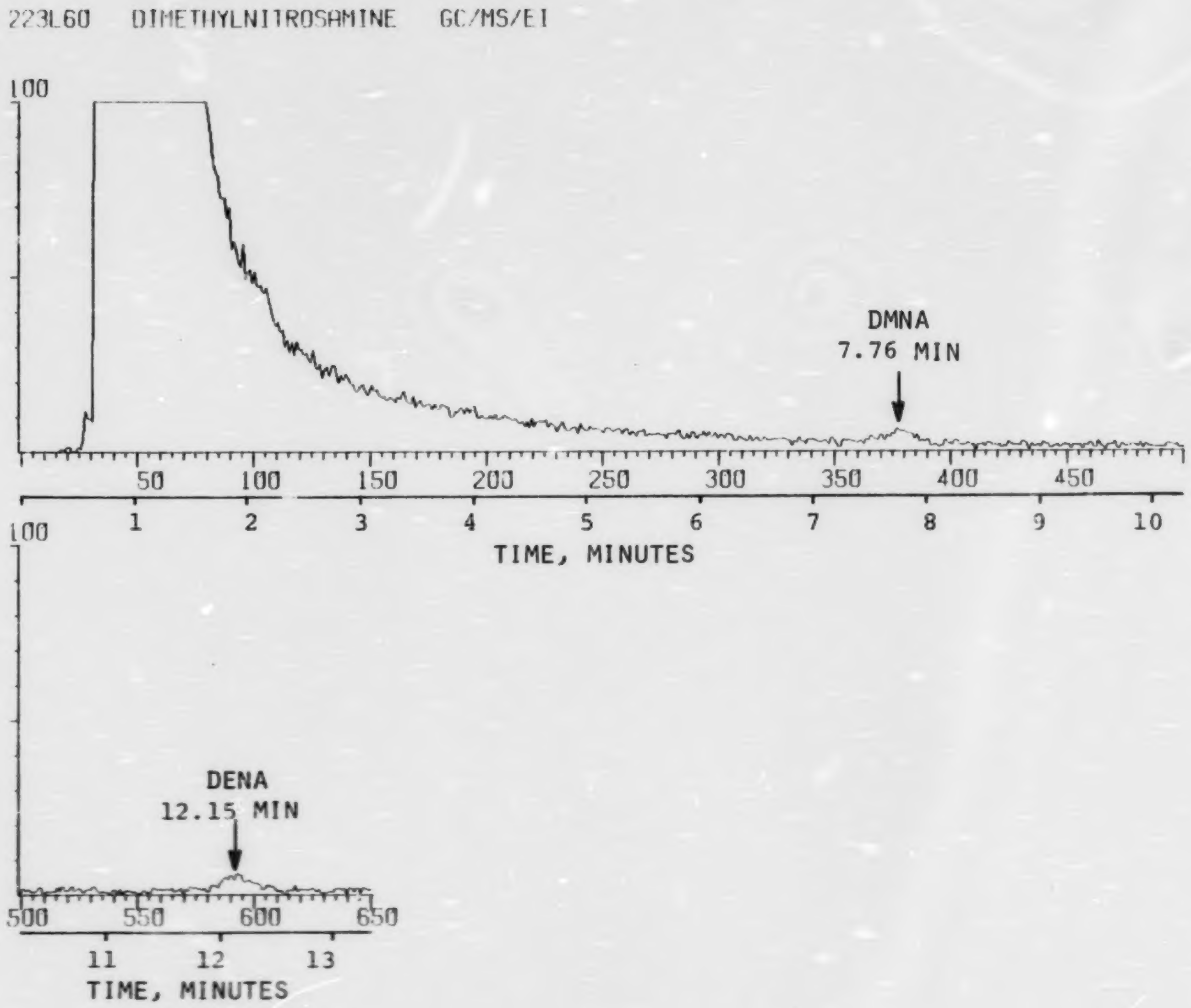


FIGURE C-2A. CHROMATOGRAM OF STANDARDS, FULL SPECTRUM SCANNING

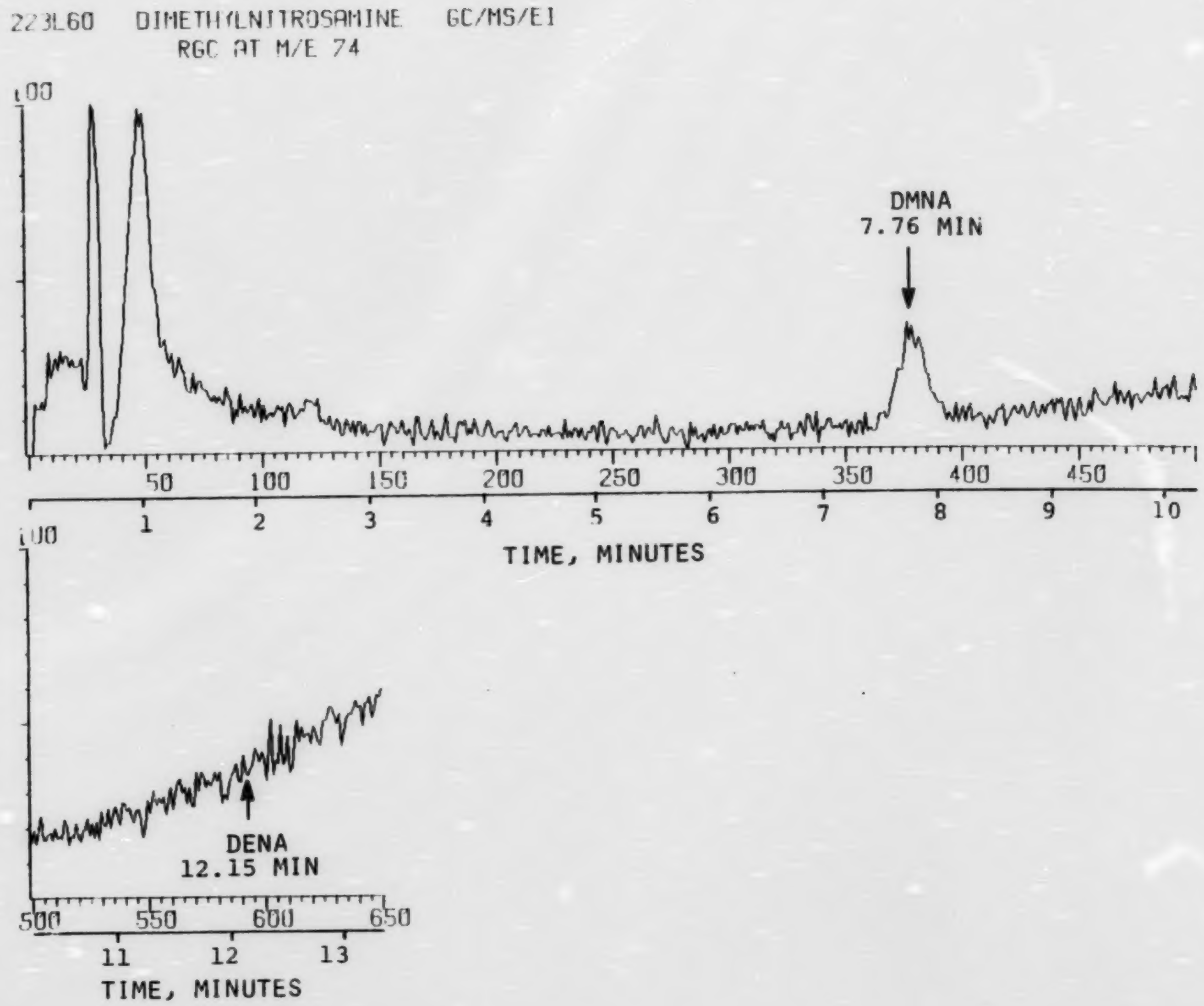


FIGURE C-2B. SINGLE ION CHROMATOGRAM COMPUTER-EXTRACTED FROM FULL SPECTRUM SCAN

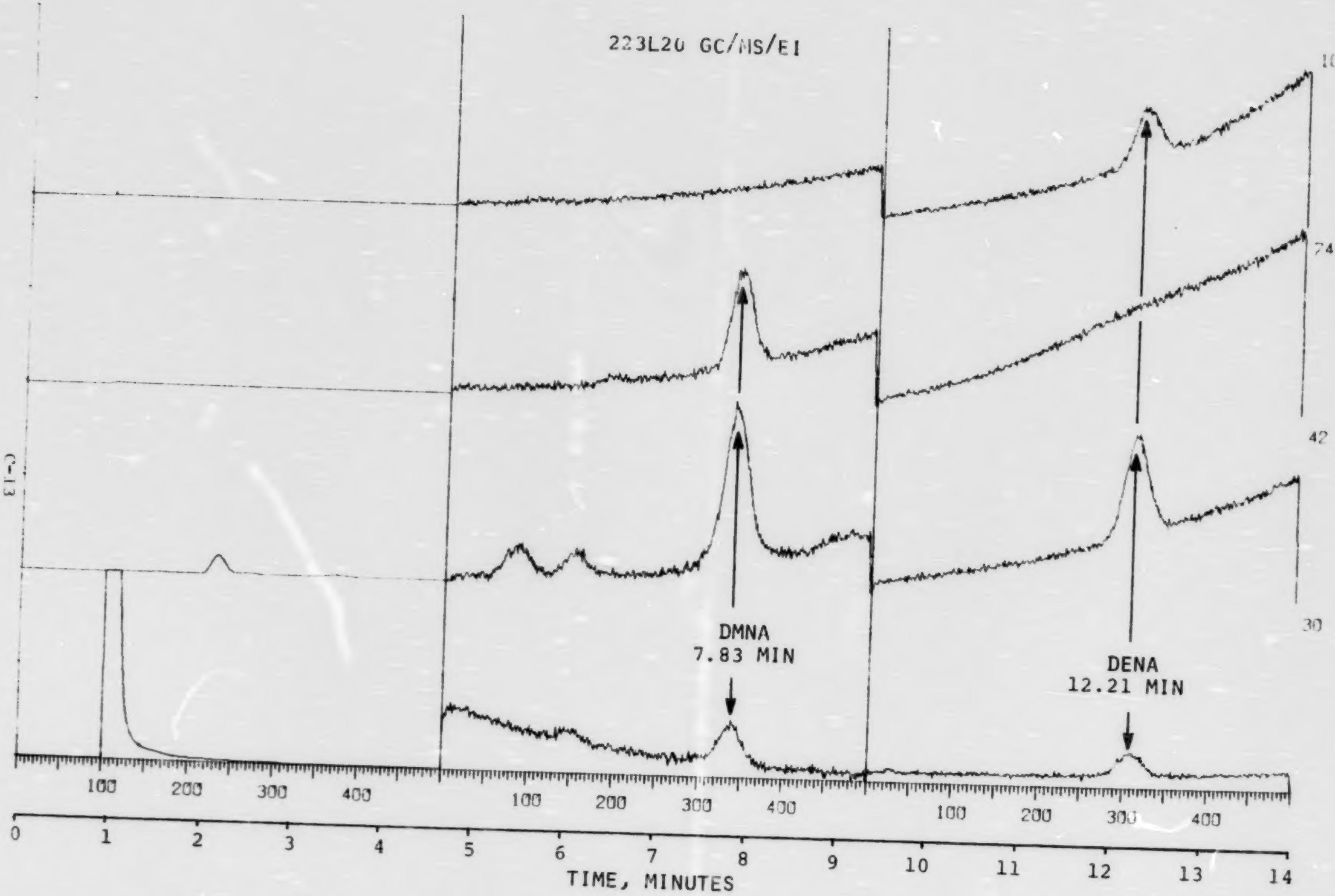


FIGURE C-3. MASS FRAGMENTOGRAM OF STANDARDS

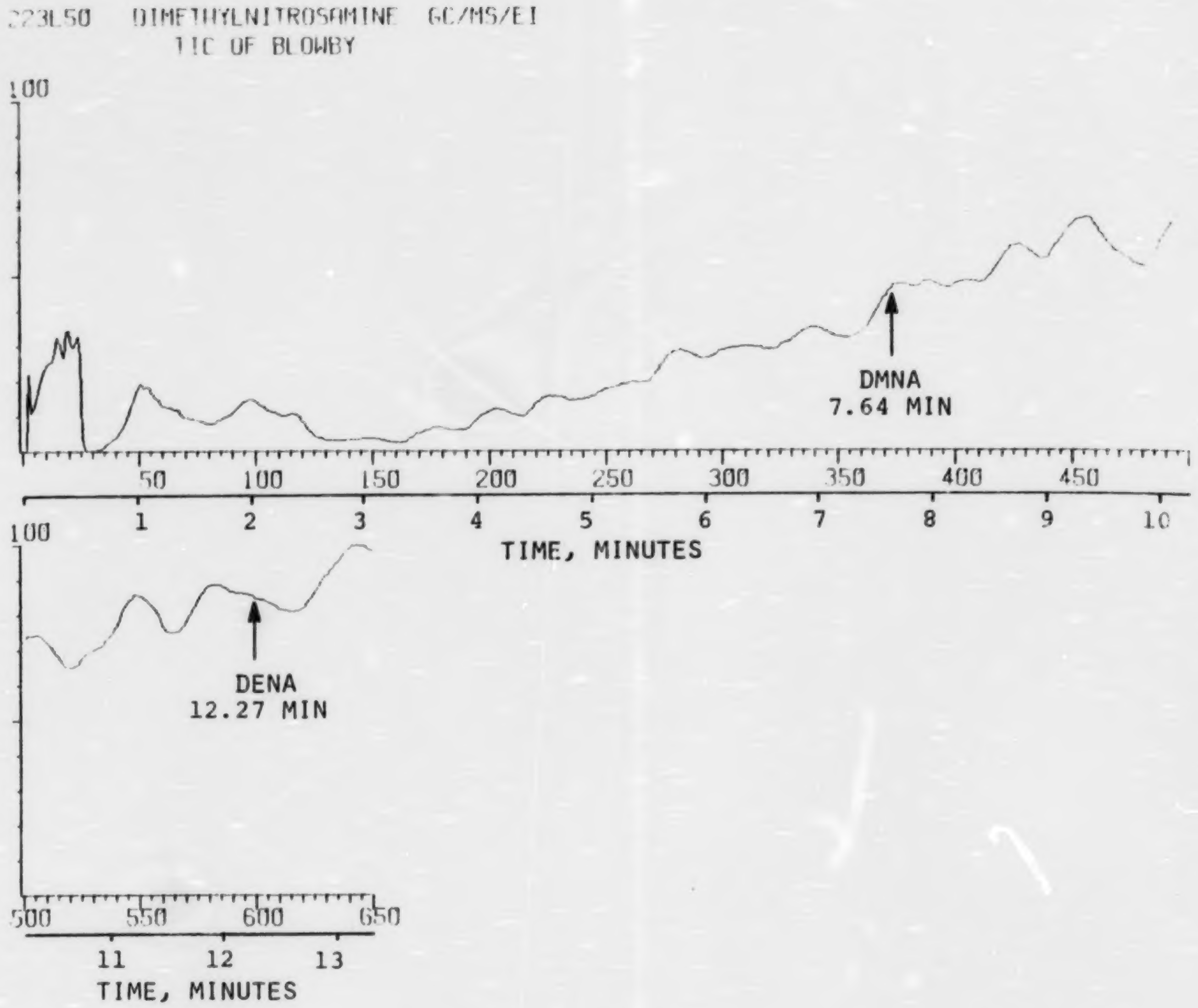


FIGURE C-4A. TOTAL ION CHROMATOGRAM OF DIESEL BLOWBY CONCENTRATE

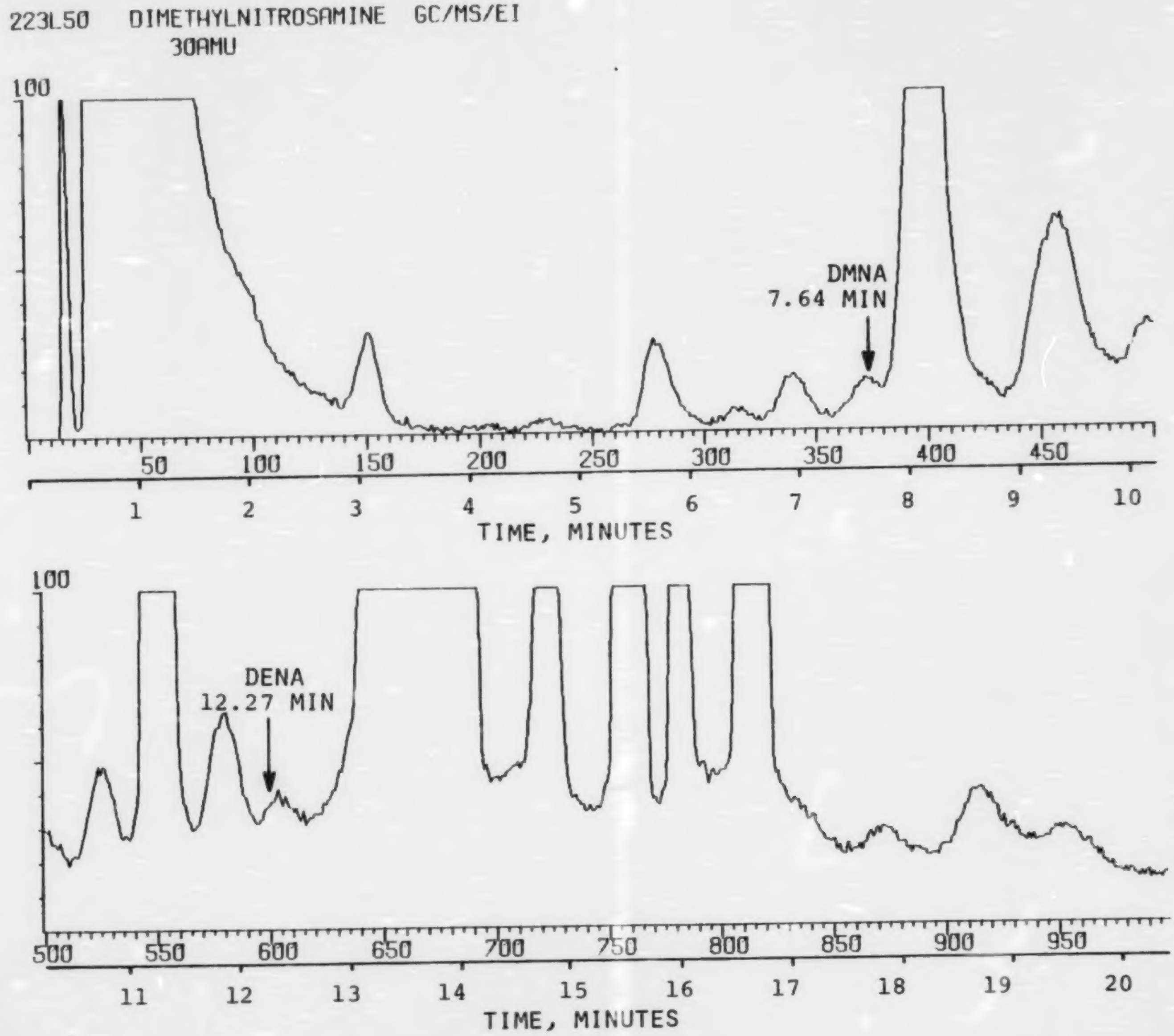


FIGURE C-4B. SINGLE ION SCANS COMPUTER-EXTRACTED FROM TOTAL ION CHROMATOGRAM

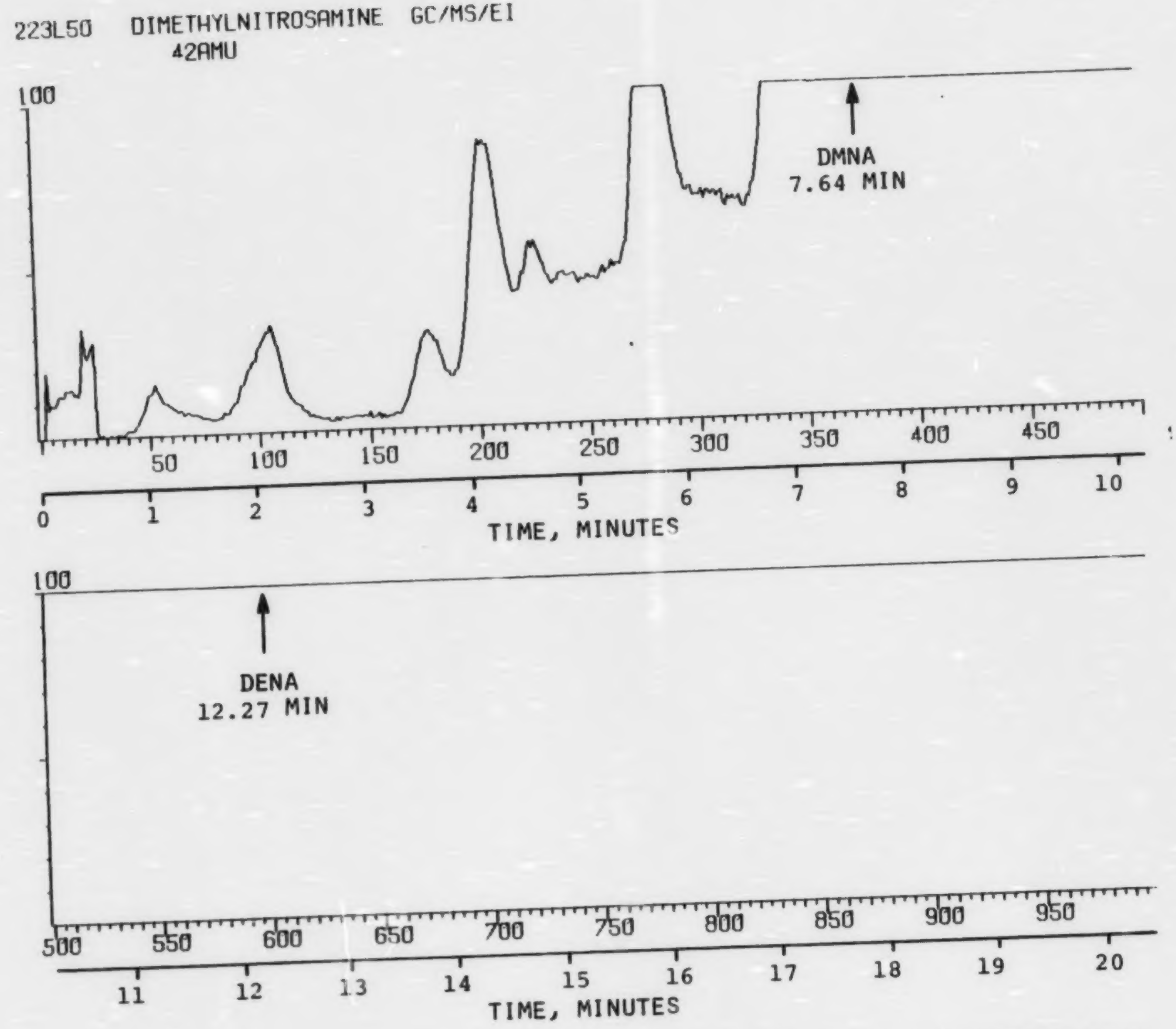


FIGURE C-4c. SINGLE ION SCANS COMPUTER-EXTRACTED FROM TOTAL ION CHROMATOGRAM

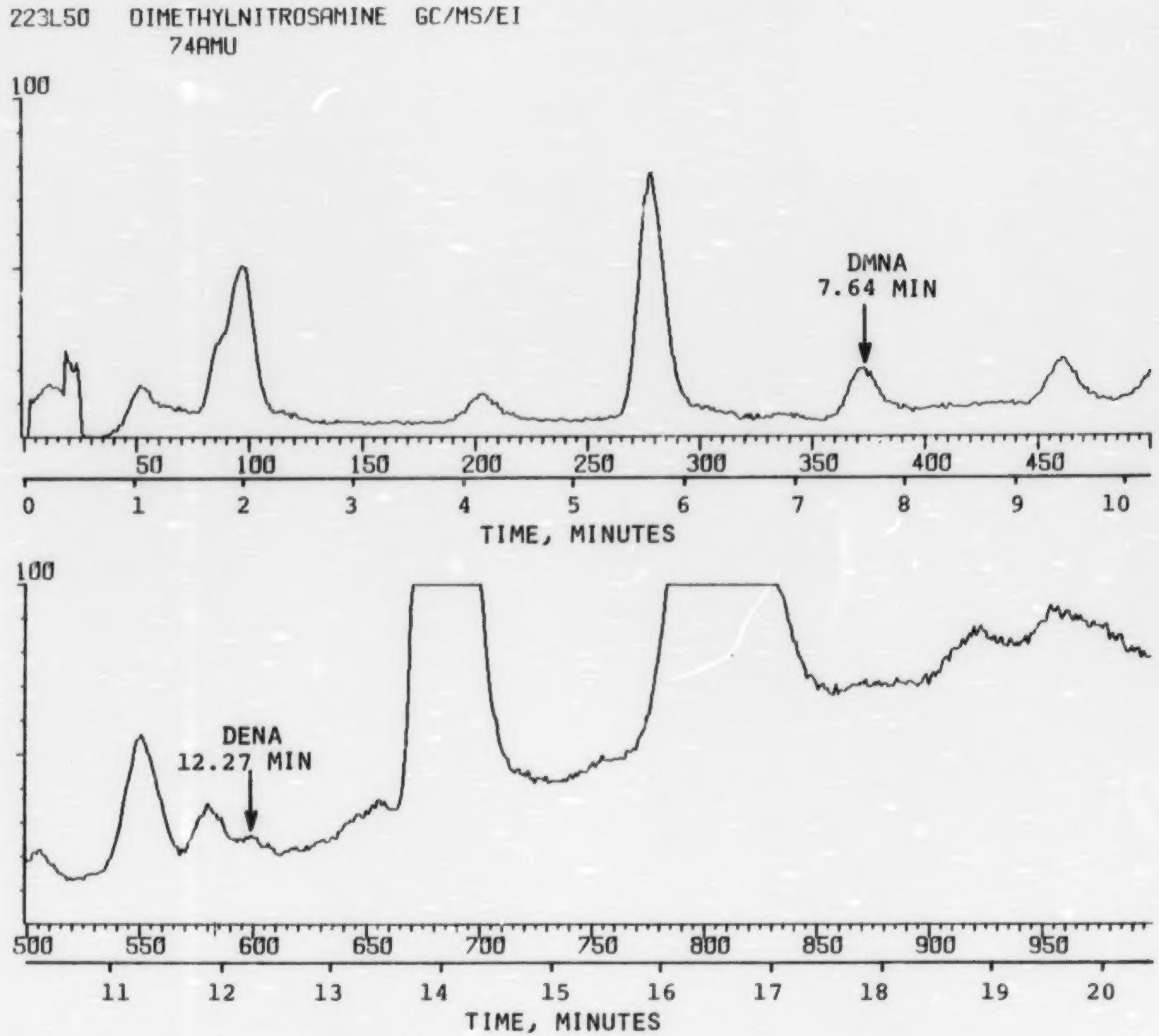


FIGURE C-4D. SINGLE ION SCANS COMPUTER-EXTRACTED FROM TOTAL ION CHROMATOGRAM

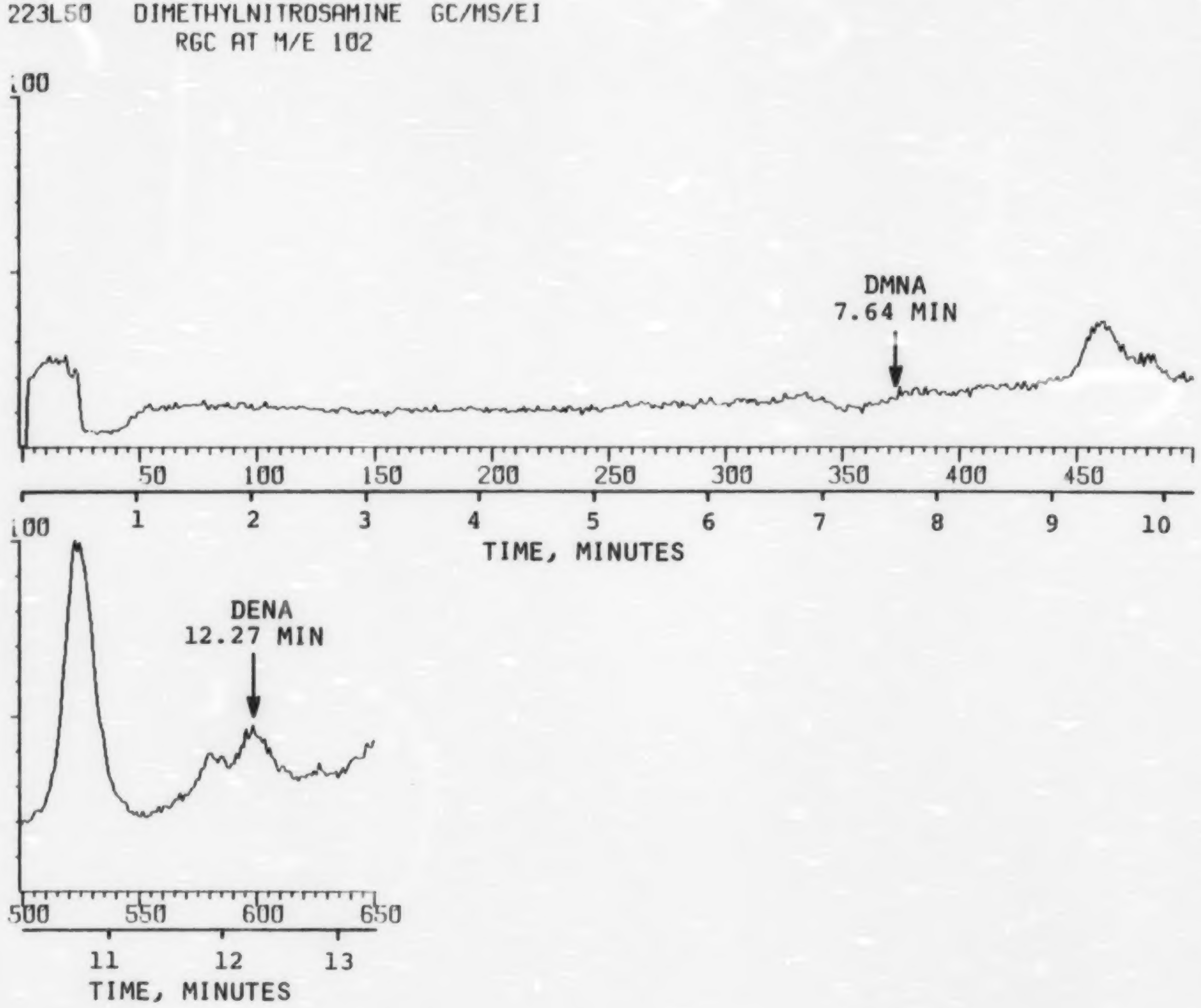


FIGURE C-4E. SINGLE ION SCANS COMPUTER-EXTRACTED FROM TOTAL ION CHROMATOGRAM

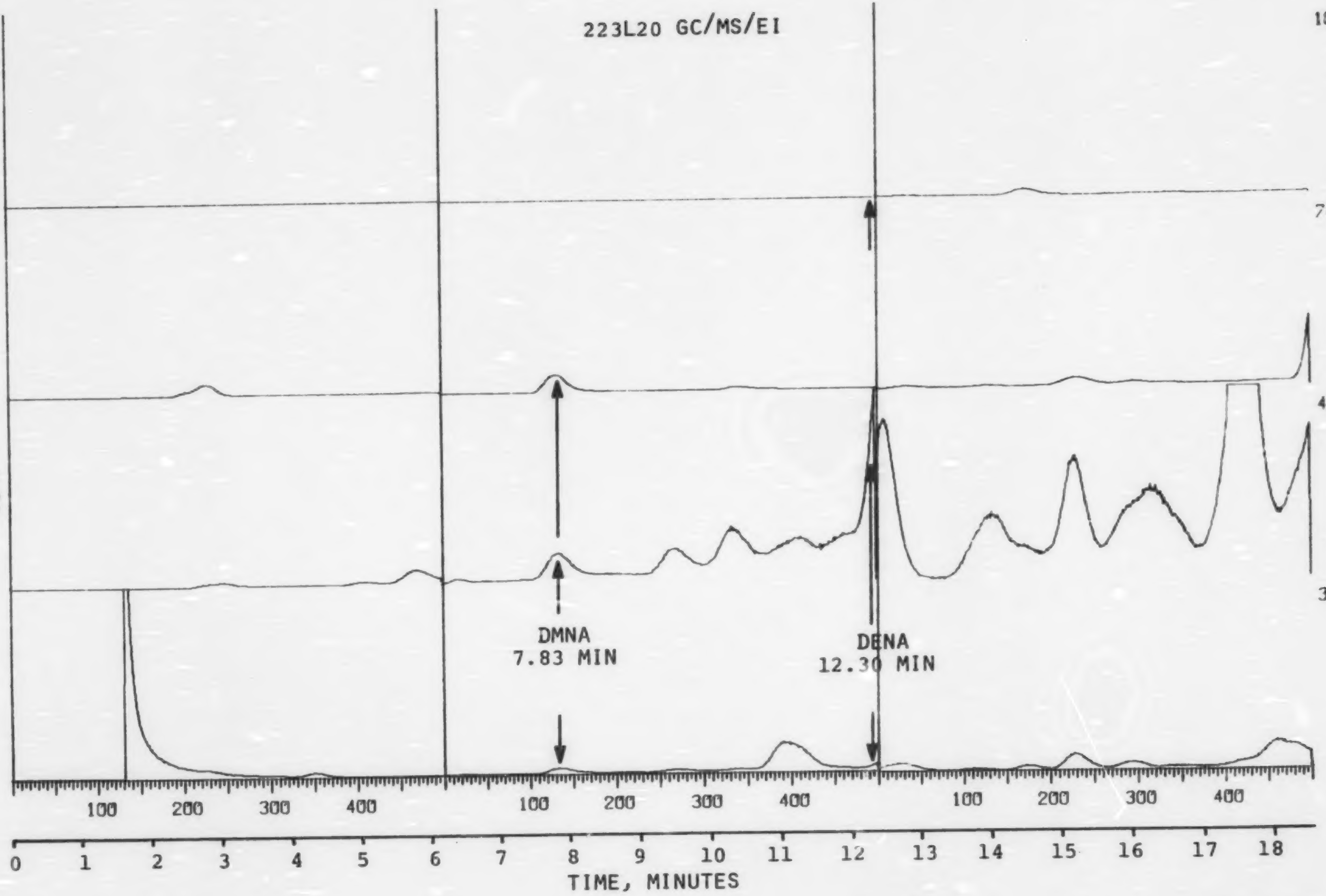


FIGURE C-5. MASS FRAGMENTOGRAM OF DIESEL BLOWBY CONCENTRATE

ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENFORCEMENT
NATIONAL ENFORCEMENT INVESTIGATIONS CENTER
BUILDING 53, BOX 25227, DENVER FEDERAL CENTER
DENVER, COLORADO 80225

TO Mr. Tom Baines
EPA - ECTD

DATE February 1, 1977

FROM Chief
Chemistry Branch

SUBJECT Results of Nitrosamine Analysis of Diesel Exhaust Samples

As discussed by phone 1/31/77, we have analyzed the methylene chloride extracts of diesel exhaust samples which you had sent to us from the Southwest Research Institute and have obtained the following results.

	Nitrosamines (ng/sample)					
Sample Description	DMN	DEN	DBN	NPIP	NMORPH	DAN
Bottle blank (1/6/77)	ND	ND	ND	ND	ND	ND
Reagent blank (1/4/77)	ND	ND	ND	ND	ND	ND
Background (1/4/77)	ND	ND	ND	ND	ND	ND
Background (1/5/77)	ND	ND	ND	ND	ND	ND
Background (1/6/77)	ND	ND	ND	ND	ND	ND
Sample (1/4/77)	45	25	17	11	51	43
Sample (1/5/77)	61	23	21	<DL	47	38
Sample (1/6/77)	54	23	19	<DL	49	ND
Detection Limits	5	5	11	8	10	24

ND = None detected
<DL = Less than detection limit

DMN = dimethyl-N-nitrosamine
DEN = diethyl-N-nitrosamine
DBN = dibutyl-N-nitrosamine
NPIP = N-nitrosopiperidine
NMORPH = N-nitrosomorphaline
DAN = diamyl-N-nitrosamine

Upon receipt, the samples were spiked with 1.0 ml of isooctane and concentrated to 1.0 ml at 60°C; 5 ul of the concentrated extracts were injected into a gas chromatograph-thermal energy analyzer system equipped with a 1/8" ID x 20' SS column packed with Carbowax 20 M + 1% KOH on 60/80 mesh Chromosorb WAW. Retention times were compared to authentic standards. In addition, a portion of sample 1/5/77 was irradiated with UV light and the peaks were found to rapidly disappear, indicating that all compounds reported are photo-labile under the same condition as authentic standards of the nitrosamines.

We would be interested to know the volume of diesel exhaust that each sample represents. Please let us know if we can be of further help to your program.

Theodore O. Meiggs, Ph.D.

cc: Blackman
Cohen

NEIC ANALYTICAL PROCEDURE FOR NITROSAMINES

Air Samples

Air samples are taken in a foil-covered impinger (SGA Catalogue #JV8550) filled with 60 ml of 1 N KOH. Sample air is drawn through the impinger by a vacuum pump and metered through a calibrated stainless steel hypodermic needle (B&D #21). Normal collection volumes range from 100 to 200 liters.

The KOH is then extracted in a 125-ml separatory funnel with three 8-ml portions of dichloromethane (Burdick and Jackson, "distilled in glass"). The combined extract is taken down to 0.5 ml on a Kuderna-Danish type assembly consisting of a three ball Snyder column attached to a specially made 50-ml concentrator flask which in turn is attached to a 4-ml calibrated receiving tube. The column and receiving tube are available through Kontes Glass Company; the 50-ml flask was custom made locally. Before taking the solution down, 0.5 ml of 2,2,4 trimethylpentane is added as a keeper. A hot water bath maintained at 58 to 60°C is used as the heat source.

All laboratory work is completed under low UV lighting; "bag" lights are used for this purpose. Typical extraction recoveries are about 40%.

Microliter aliquots of the concentrates are then injected into a gas chromatograph attached to a Thermo Electron Corporation Thermal Energy Analyzer. A dry ice/acetone mixture is used in the cold trap on the TEA. The GC column used is 20 ft. 1/8 inch O.D. stainless steel with 15% FFAP on 60/80 mesh Chromsorb WAW DCMS. Typical injection volumes are 5 μl.

Water Samples

Grab samples are collected in amber glass quart bottles with teflon liners. Two 50-ml portions of dichloromethane are used to extract the sample in a 2000-ml separatory funnel. The combined extract is taken down as above, only using a 250-ml concentrator flask and 1 ml of 2,2,4 trimethylpentane is added as a keeper before concentration. In some cases it may not be necessary to concentrate to 1 ml in order to obtain measurable amounts of nitrosamines. Similarly, it is advisable to keep volumes injected into the GC/TEA as small as possible.

Granular anhydrous sodium sulfate (Mallinkrodt AR) may be used to treat emulsions during the extractions. Its freedom from interfering materials should be established by running several blanks.

Richard C. Ross
Chemistry Branch

ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK

TO: Charles T. Hare, SwRI
FROM: Roy Zweidinger, EPA
DATE: May 26, 1977
SUBJECT: Diesel Blow-by Samples

Enclosed are the spectra obtained from the ion chromatographic analysis of the diesel blow-by samples sent by SwRI. Spectra of several amines and other cations are included. Retention times are written above each peak.

Na^+, NH_4^+ and K^+ appear to be the only detectable ions, however methylamine and ethanolamine could be present and obscured by the NH_4^+ and K^+ peaks.

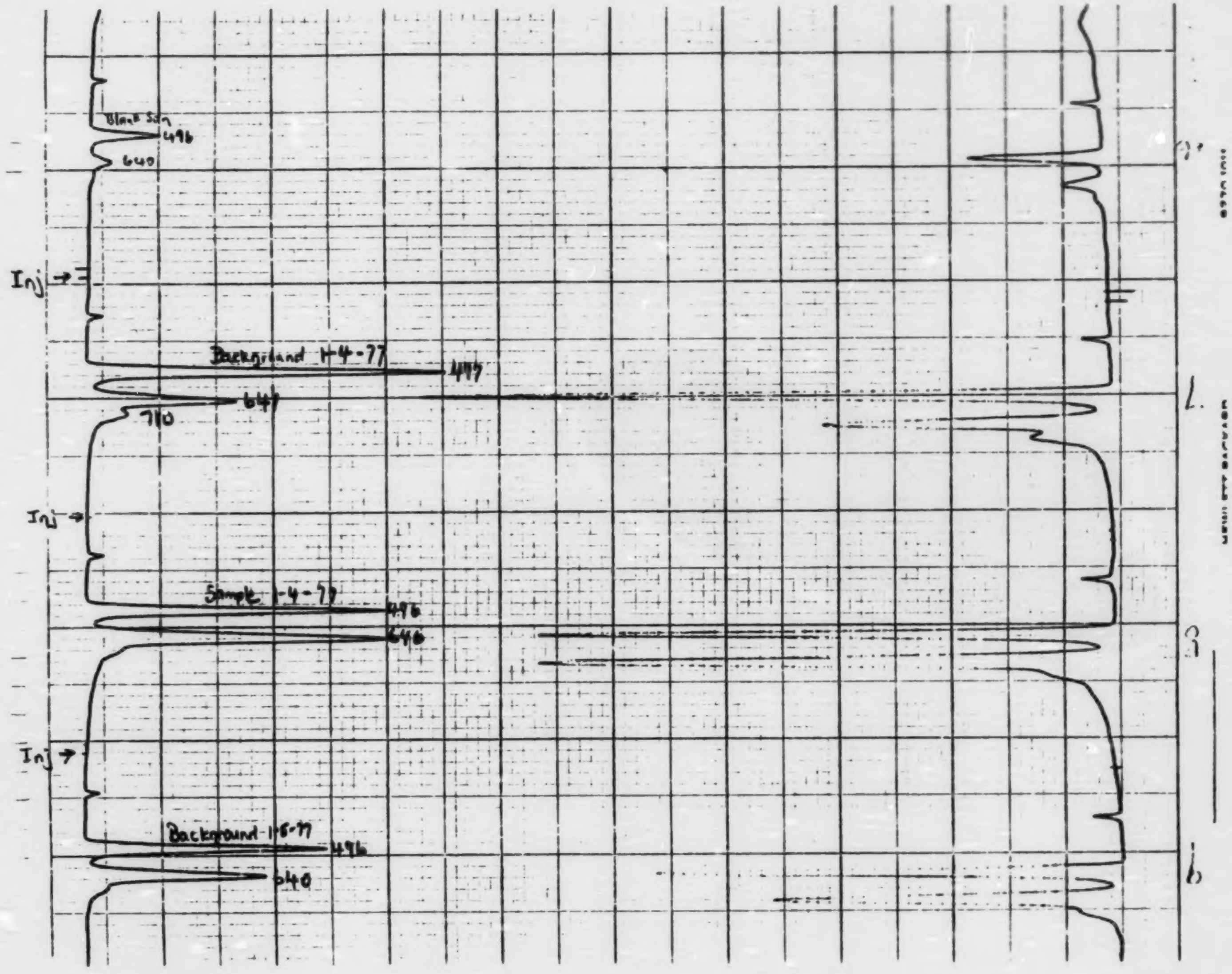


FIGURE C-6. ION CHROMATOGRAM OF MACK ETAY(B)673-A CRANKCASE GAS SAMPLES, BLANK, AND BACKGROUND AIR

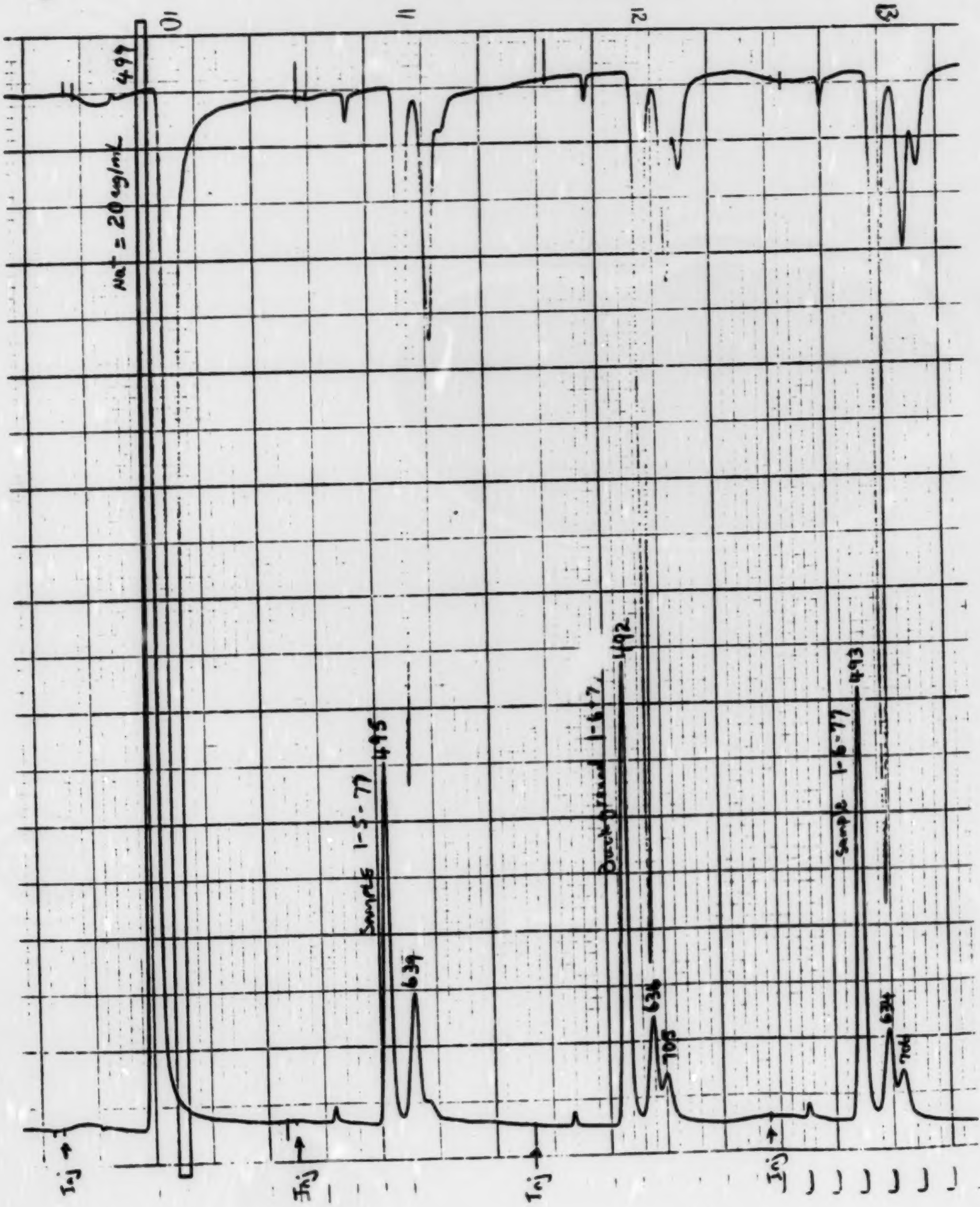


FIGURE C-7. ION CHROMATOGRAM OF MACK ETAY(B)673-A CRANKCASE GAS SAMPLES, BACKGROUND AIR, AND NA+ STANDARD

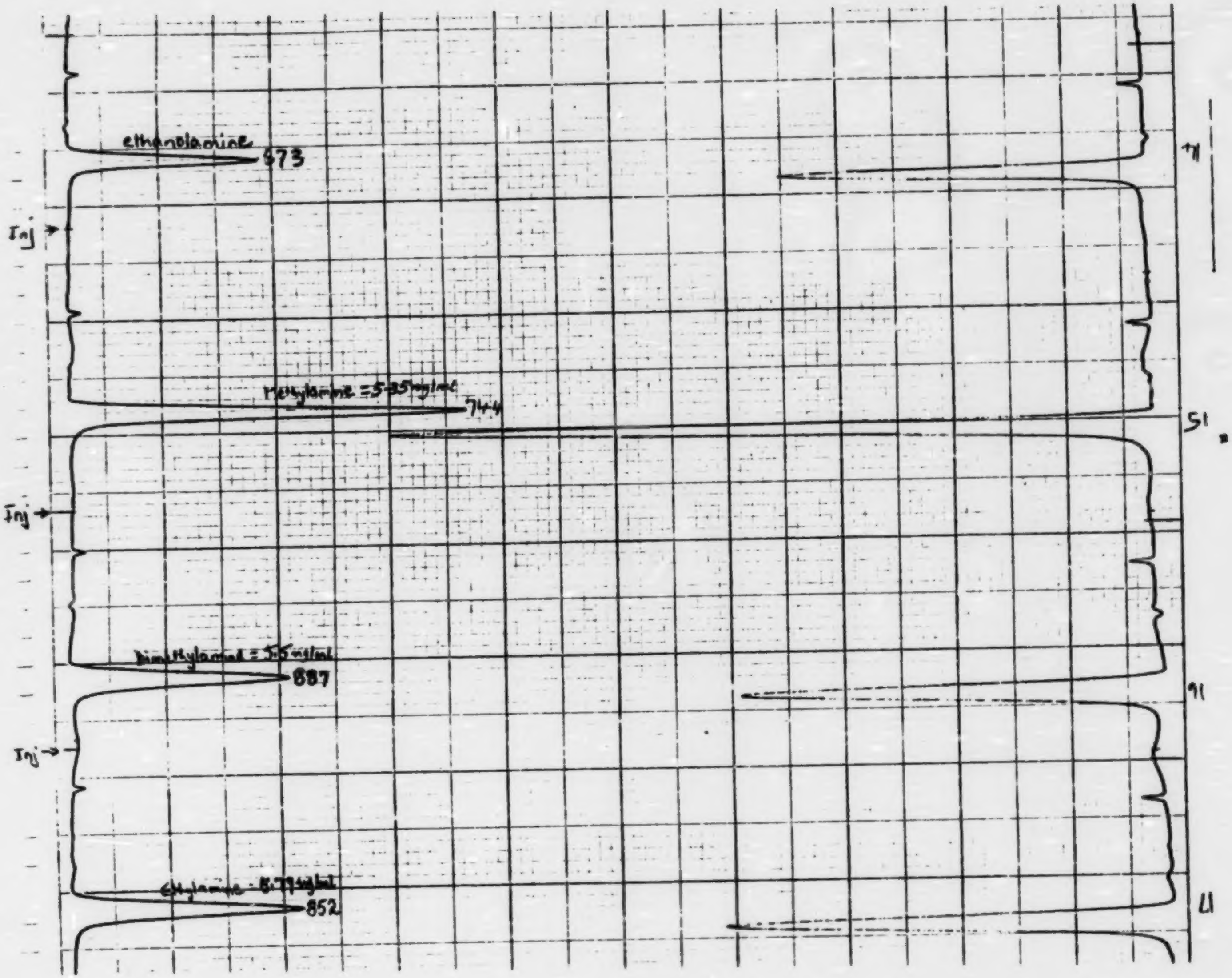


FIGURE C-8. ION CHROMATOGRAM OF AMINE STANDARDS

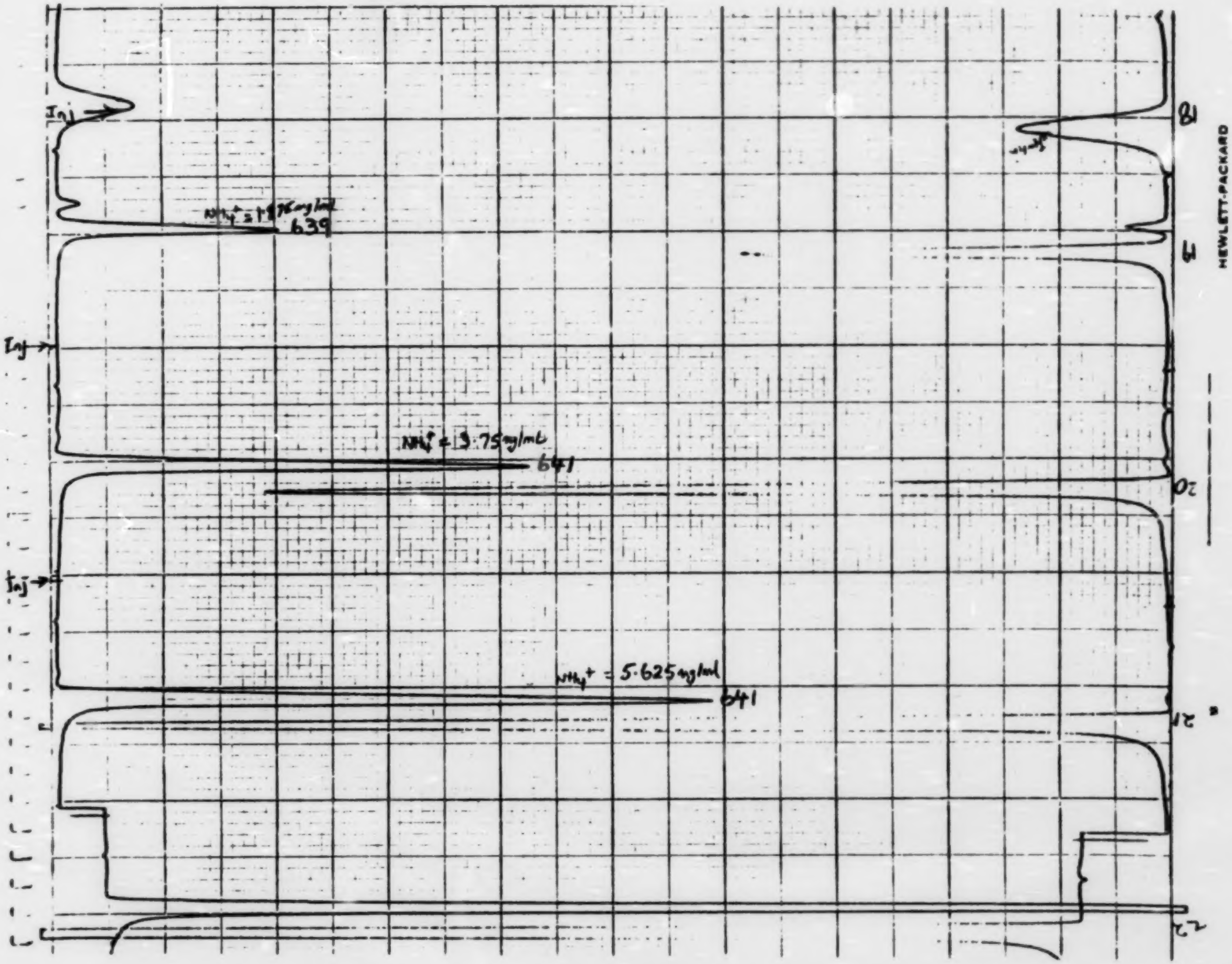


FIGURE C-9. ION CHROMATOGRAM OF NH_4^+ STANDARDS

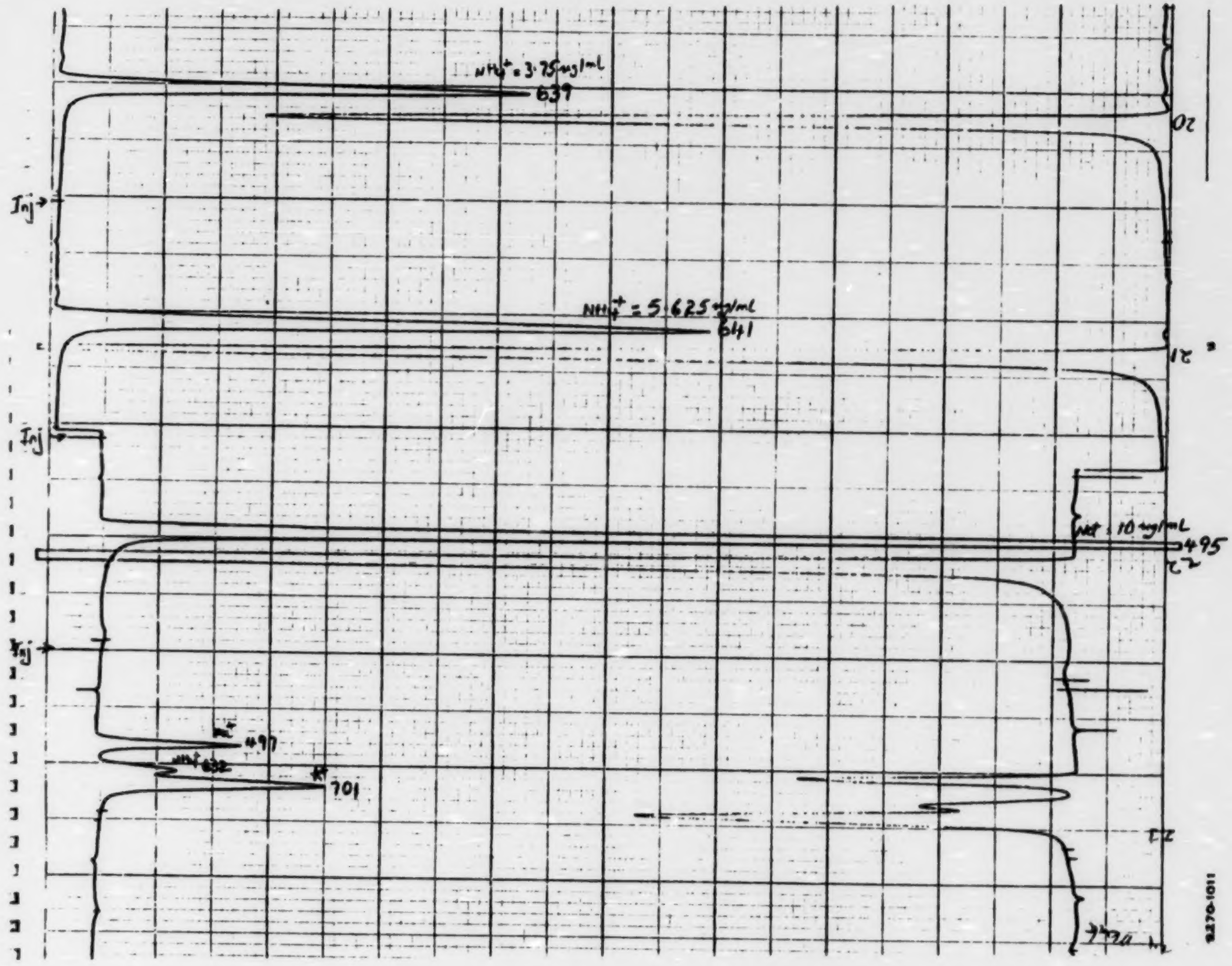


FIGURE C-10. ION CHROMATOGRAM OF NH_4^+ AND Na^+ STANDARDS

SOUTHWEST RESEARCH INSTITUTE
8500 CULEBRA ROAD • POST OFFICE DRAWER 28510 • SAN ANTONIO, TEXAS 78284

February 14, 1977

Dr. Edo Pellizzari
Research Triangle Institute
Cornwallis Road
PO Box 12194
Research Triangle Park, NC 27709

Dear Edo:

This will confirm our telephone conversation regarding diesel crankcase gaseous samples taken on February 11, 1977. The following lists the quantity of crankcase vapor diluted in a premeasured amount of zero-grade dry N_2. In the case of the "1 liter" samples, the premeasured amount was 0.44 cu ft (12.46 liter) of N_2, while the "5 liter" samples were added to a premeasured 2.2 cu ft (62.3 liter) of N_2. In both cases, assuming 1 liter and 5 liter samples were taken, the target dilution level was 13.5.

The 13.5 dilution level would then result in the nominal 60 ppm NO_x raw vent gas concentration being reduced to about 4.8 ppm. We wanted to get below 5 ppm without excessive dilution. As mentioned, the sample rate from the engine was a nominal 1 liter/min monitored and timed by a Brooks flowmeter and stop watch. The engine crankcase was backpressured slightly (approximately 0.4 in H_2O) to force the sample through a 3/8 inch OD stainless probe that was connected to the flowmeter. The sample probe was 8 inches long and was unheated. It was inside a larger pipe fitting which connected to the crankcase vent through which the remainder (most) of the vent gases passed around the probe and then to atmosphere via a gate (backpressure) valve.

No external heating was employed and only the flowmeter was open to the cell ambient. No water or oily condensate was noted. I estimate the sample gas temperature at the inlet to the flowmeter to be on the order of 100-125 °F.

New Tedlar sample bags were used for each sample. First, about 0.5 cu ft N_2 was added to the evacuated bag, and then the bag was evacuated to a vacuum of 10 inches water. Then the desired amount of N_2 diluent was added, metered by a wet test meter. This bag was then connected to the sample flowmeter outlet and the crankcase gases were added at a 1 liter/min rate into the bag. The contents of the bag were thoroughly mixed for about 1 minute. The bag was then connected to the items you furnished; namely, the fiberglass prefilter, the cartridge holder and then our pump, a flowmeter, and finally the same wet test meter. The amount of sample was calculated by subtracting the N_2 from the N_2 + sample column. A new prefilter was used for each sample.

Prior to taking samples for record, the sampling and cartridge loading procedures were thoroughly developed to assure that what was added to the bag could be accurately metered to give a close value for sample amount. The system was leak-checked and precalibrated.

When loading the cartridge, a flow of 7.7 liter/minute was maintained constant and continued until the bag was evacuated to 10 in H_2O vacuum. The withdrawal time was approximately 1.7 minutes for bags containing 1 liter and 8.7 minutes for bags containing 5 liter of sample.

By copy of this letter, I am informing Tom Baines and Ron Bradow of the technique we used and the basic sampling data. We are very interested in your findings with these cartridges.

Very truly yours,

Karl J. Springer

Karl J. Springer
Director
Department of Emissions Research

KJS:cp
cc: Tom Baines
Ron Bradow

TABLE 1. CRANKCASE GAS SAMPLING DATA - TENAX GC CARTRIDGES MACK ETAY(B) 673A

Date: 2/11/77 Fuel: EM-239-F
Gulf 2D @ 0.23% S

Cart No.	N_2 Diluent				Cartridge Load				Crankcase Sample			Dilution Ratio[2]
	Volume, obs ft^3	Volume, obs ℓ	Temp °F	P_{Bar} in Hg	Volume, obs ft^3	Volume, obs ℓ	Temp °F	P_{Bar} in Hg	Volume, obs ft^3	Volume, obs ℓ	Corr[1] ℓ	
	Nominal 1 liter Sample											
1	0.44	12.46	74	29.105	0.472	13.365	74	29.105	0.032	0.906	0.789	14.75
2	0.44	12.46	74	29.088	0.479	13.563	75	29.088	0.029	0.821	0.713	16.52
3	0.44	12.46	76	29.083	0.469	13.280	76	29.083	0.029	0.830	0.718	16.0
	Nominal 5 liter Sample											
4	2.2	62.3	76	29.071	2.368	67.053	77	29.071	0.168	4.765	4.109	14.07
5	2.2	62.3	77	29.071	2.386	67.562	77	29.071	0.186	5.275	4.549	12.81
6	2.2	62.3	77	29.072	2.382	67.449	77	29.072	0.182	5.154	4.444	13.09

[1] Corrected ℓ

$V_s = \frac{T_s}{T_m} \frac{P_m}{P_s} V_m$, S = std T & P of 32 °F & 29.92 in Hg
m = Meter Conditions

Note manometer reading of Wet Test Meter = 0.20 in H_2O

Example: $V_s = \frac{460 + 32}{460 + 74} \left(\frac{29.105 + (0.20) \quad (.074) - 0.838}{29.92} \right) 0.906\ell = 0.789\ell$

where the 0.838 is water vapor pressure, in Hg @ 74°F and 29.0 in Hg Bar.

[2] Dilution Ratio = $\frac{\text{Dilution Vol + Sample Vol}}{\text{Sample Vol}} = \frac{\text{Cartridge Load (observed)}}{\text{Sample Vol (observed)}}$

RTI

RESEARCH TRIANGLE INSTITUTE

EPA Contract No. 68-02-2262

RTI Project No. 31U-1208

Interim Report

Date: April, 1977

ANALYSIS OF BLOW-BY GAS FROM DIESEL CRANK CASE VENT FOR N-NITROSOAMINES AND OTHER VOLATILE ORGANIC VAPORS

by

E Pellizzari

E. D. Pellizzari, Ph.D.

Chemistry and Life Sciences Division
Research Triangle Institute
P. O. Box 12194
Research Triangle Park, North Carolina 27709

Prepared for Environmental Protection Agency, Research Triangle Park, North Carolina 27711

1.0 Introduction

Because of the interest in the possible formation or presence of nitrosamines in the blow-by gas (crank case vent) from diesel engines, a study was conducted to determine whether their existence could be verified. Other research tentatively detected N-nitrosodimethylamine in the Eisenhower Tunnel in Colorado. Its detection was reported by two independent research groups.(1,2) This observation precipitated a search to determine the origin of DMN. In previous studies, it had been established that N-nitrosodimethylamine was not present in auto exhaust.(3)

Since DMN was not observed in auto exhaust, other possibilities were examined. These were diesel exhaust and the blow-by gas from diesel crank cases. A collaborative study was initiated between the Environmental Protection Agency (EPA), RTP; EPA, Ann Arbor, MI; Southwest Research Institute (SRI) and the Research Triangle Institute (RTI). Since SRI was under contract to examine and characterize diesel engine performance, a study on the blow-by gas was conducted for N-nitrosodimethylamine.

2.0 Methods of Analysis

2.1 Collection of Organic Vapors in Blow-by Gas (Conducted by SRI)

The method for collecting organic vapors in blow-by gas from diesel crank cases utilized the RTI Tenax GC cartridge which had been previously reported for sampling of ambient air in organic vapors and auto exhaust.(1,3-6)

Since the nominal NO_x raw vent gas concentration is approximately 60 ppm, a dilution step was utilized to reduce the NO_x level to 5 ppm or less. This step was instituted since it was uncertain whether in situ reactions between NO_x and dimethylamine if present in the raw vent gas would produce N-nitrosodimethylamine at NO_x levels above 5 ppm. Previous research at RTI had indicated that sampling of gases with NO_x levels below 5 ppm did not contribute to the in situ formation of DMN.(1)

Diesel crank case gaseous samples were taken at two levels. One liter and 5 ℓ samples of blow-by gas were obtained by premeasuring an amount of ~0.44 ft^3 (12.46 ℓ) and 2.2 ft^3 (62.3 ℓ) of nitrogen, respectively, into Tedlar® bags. In both cases assuming 1 and 5 ℓ samples being taken, the target dilution level would be 13.5.

The 13.5 dilution level thus produced a reduction of the 60 ppm NO_x to about 4.8 ppm. The sampling rate from the engine crank gas was a nominal 1 ℓ/min as monitored by a Brooks flow meter and stopwatch. In order to acquire a sample, the engine crank case was back pressured slightly (~0.4" of water) to force the sample through a 3/8" o.d. stainless probe that was connected to the flow meter. The sample probe was 8" long and was unheated. It was inside a larger pipe fitted to the crank gas vent through which the remainder, mostly vent gas, passed around the probe to the atmosphere via a gate (back pressure) valve.

No external heating was employed and only the flow meter was opened to the cell ambient. As reported by Southwest Research Institute, no water or oily condensate was noted. The sample gas temperature at the inlet to the flow meter was estimated to be in the order of 100-125°F.

New Tedlar sample bags were used for collecting each sample. To begin with, ~0.5 m^3 ft of nitrogen was added to an evacuated bag and then the bag was evacuated to a vacuum of 10" of water. Then the desired amount of nitrogen diluent was added, metered by a wet test meter. This bag then was connected to the sample flow meter outlet and the crank case gases were added to a 1 ℓ/min rate into the bag. The content of the bag was thoroughly mixed for about 1 min and then connected to the sampling train which consisted of a glass fiber pre-filter, cartridge holder (Tenax GC), a pump flow meter and finally to a wet test meter. The amount of sample was calculated by subtracting the nitrogen from the nitrogen plus sample column. A new pre-filter was used for each sample taken.

During the passage of the diluted crank case vent gas through the Tenax GC sampling cartridge, a flow of 7.7 ℓ/min was maintained and continued until the bag was completely evacuated down to 10" of water vacuum. The withdrawal time was ~1.7 min for bags containing 1 ℓ and 8.7 min for bags containing 5 ℓ/sample.

Table 1 lists the pertinent data provided by SRI associated with the crank gas sampling utilizing the Tenax GC cartridges.

2.2 Sample Analysis

Samples received from Southwest Research Institute were analyzed by mass chromatography utilizing previously described procedures.(1) The instrumental system (glc/ms) for the quantitative analysis of

Table 1. CRANKCASE GAS SAMPLING DATA - TENAX GC CARTRIDGES
MACK ETAY(B) 673A (SRI DATA)

Date: 2/11/77 Fuel: EM-239-F
Gulf 2D @ 0.23% S

Cart No.	N_2 Diluent Volume, obs ft³	N_2 Diluent Volume, obs ℓ	N_2 Diluent Temp °F	N_2 Diluent P_{Bar} in Hg	Cartridge Load Volume, obs ft³	Cartridge Load Volume, obs ℓ	Cartridge Load Temp °F	Cartridge Load P_{Bar} in Hg	Crankcase Sample Volume, obs ft³	Crankcase Sample Volume, obs ℓ	Crankcase Sample Corr ℓ (1)	Dilution Ratio (2)
					Nominal 1 liter Sample							
1	0.44	12.46	74	29.105	0.472	13.365	74	29.105	0.032	0.906	0.789	14.75
2	0.44	12.46	74	29.088	0.479	13.563	75	29.088	0.029	0.821	0.713	16.52
3	0.44	12.46	76	29.083	0.469	13.280	76	29.083	0.029	0.830	0.718	16.0
					Nominal 5 liter Sample							
4	2.2	62.3	76	29.071	2.368	67.053	77	29.071	0.168	4.765	4.109	14.07
5	2.2	62.3	77	29.071	2.386	67.562	77	29.071	0.186	5.275	4.549	12.81
6	2.2	62.3	77	29.072	2.382	67.449	77	29.072	0.182	5.154	4.444	13.09

(1) Corrected ℓ

$V_s = \frac{T_s}{T_m} \frac{P_m}{P_s} V_m$, S = std T & P of 32 °F & 29.92 in Hg
m = Meter Conditions

Note manometer reading of Wet Test Meter = 0.20 in H_2O

Example: $V_s = \frac{460 + 32}{460 + 74} \left(\frac{29.105 + (0.20) \quad (.074) - 0.838}{29.92} \right) 0.906\ell = 0.789\ell$

where the 0.838 is water vapor pressure, in Hg @ 74°F and 29.0 in Hg Bar.

(2) Dilution Ratio = $\frac{\text{Dilution Vol + Sample Vol}}{\text{Sample Vol}} = \frac{\text{Cartridge Load (observed)}}{\text{Sample Vol (observed)}}$

N-nitrosodimethylamine in the inlet manifold for recoverying vapors trapped on Tenax GC cartridge samplers have been described.(1,3-6) The operating conditions for the inlet-manifold were as follows: desorption chamber 265°C; six-port valve, 275°C; cryogenic trapping, -195°C; injection, 180°C; thermal desorption time, 4 min. Gas-liquid chromatography was on a 48 m glass SCOT capillary coated with DEGS in 0.1% of benzyltriphenylphosnonium chloride. The capillary column was programmed from 70-205°C at 4°/min and the carrier gas flow (helium) was 1.5 ml/ min. A single stage glass jet separator (220°C) interfaced the SCOT capillary column to the mass spectrometer. The mass spectrometer (Varian MAT CH-7 620L computer) conditions were filament current, 300 μg; ion source vacuum, 2×10^{-6} torr; magnetic current to monitor m/e 74. The intensity of m/e 74 was recorded vs time.

Standards of DMN were used for determining the response of the mass spectrometer (area 4 m/e 74 peak at retention time for DMN) vs the concentration of DMN was obtained. Air DMN vapor was synthesized and specific quantities collected on Tenax GC cartridges. The cartridges were then desorbed and the m/e 74 ion monitor to obtain detector response vs concentration. Based on the volume of air sampled, the concentration of N-nitrosodimethylamine was calculated in ng/m^3 of ambient air.

3.0 Results and Discussion

The Tenax GC sampling cartridges which were used to collect volatile organic vapors including N-nitrosoamines were subjected to gc/ms analysis. Two cartridges corresponding to samples No. 1 and 4 (1 and 5 ℓ of blow-by gas) were analyzed by single ion monitoring (m/e 74) for N-nitrosodimethylamine. Figure 1 depicts a mass chromatogram for 25 ng of N-nitrosodimethylamine. The retention time was 19.5 min. The maximum limit of detection was observed to be ~0.5 ng.

Figures 2 and 3 present the mass chromatograms for samples Nos. 1 and 4 of diesel blow-by gas. As indicated in each figure by the arrow at 19.5 min, no N-nitrosodimethylamine was detected. Sample No. 1 (Table 1, Fig. 2) was run at an attenuation of 0.1 V which represents the limit of detection for the instrumentation. Thus, if DMN was present on the sampling cartridge it was below 0.5 ng or ~166 ppt in the blow-by gas. Sample No. 4 (Table 1, Fig. 3) represented ~5 ℓ of blow-by gas and in this case the detection limit was ~100 ppt.

Since no DMN was detected in either the 1 or 5 ℓ samples of diesel blow-by gas, we proceeded to examine sample No. 6 under acquisition of full mass spectra. Sample No. 6 was subjected to gas chromatography/mass spectrometry/computer analysis utilizing the same chromatographic column (48 m SCOT DEGS) that was used in the previous analyses. Table 2 presents the results of the volatile organic vapors which were identified in sample No. 6. Although these constituents were not quantitated, the major components as observed by the total ion current profile were phenol and N,N-dimethylacetamide. It was estimated that these two components comprised ~30% of all of the observed constituents. The primary reason for the analysis of sample No. 6 was to determine whether

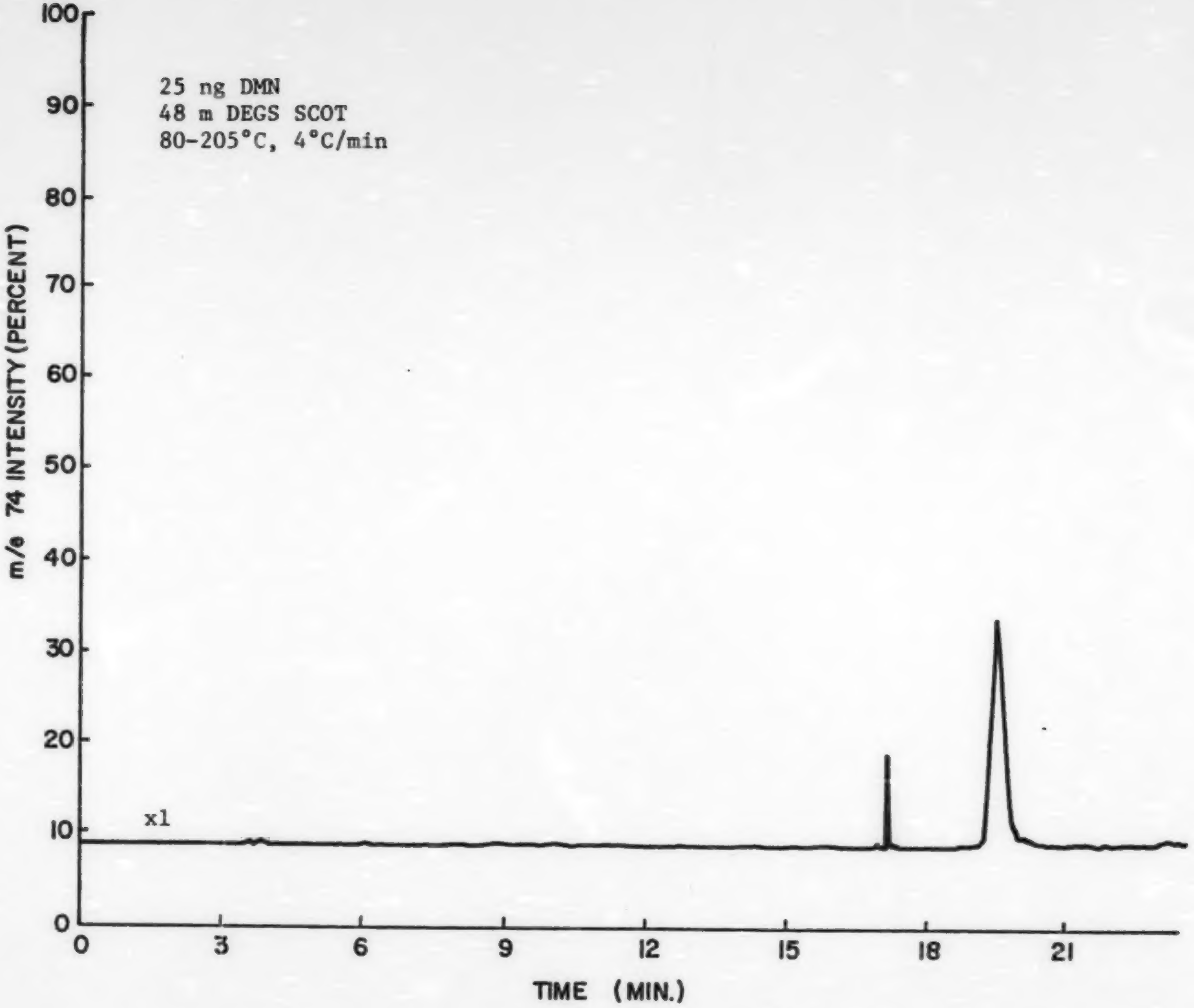


Figure 1. Mass chromatogram of N-nitrosodimethylamine.

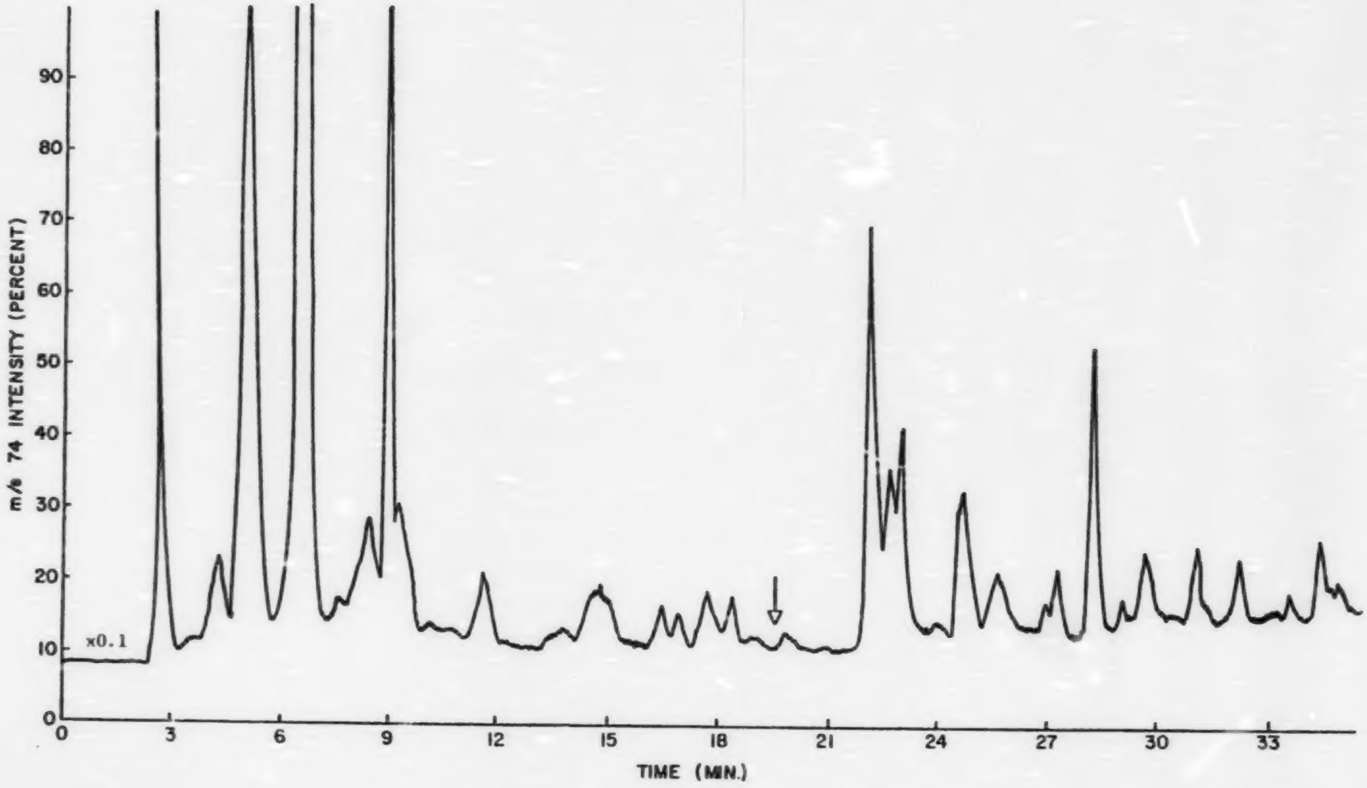


Figure 2. Mass chromatogram of sample No. 1 of diesel blow-by gas.

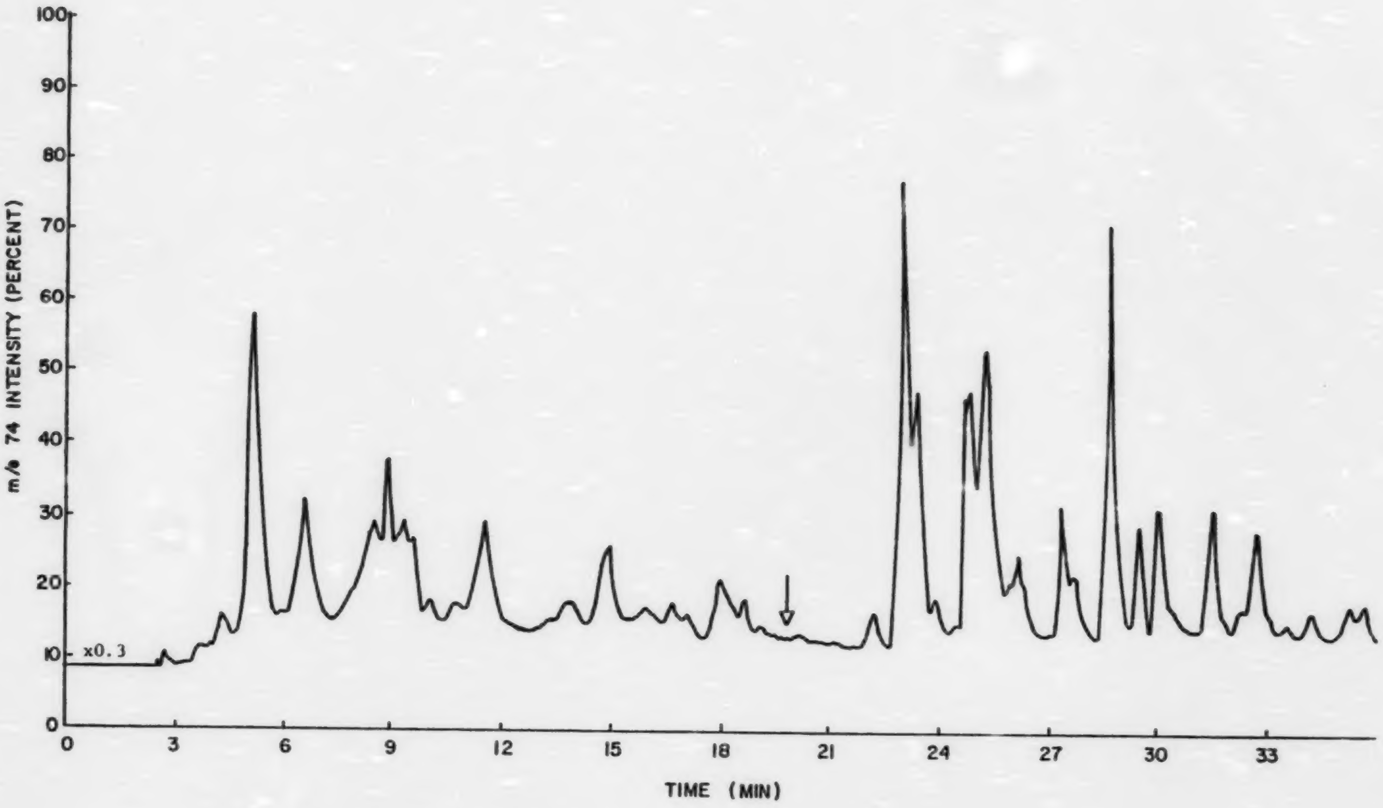


Figure 3. Mass chromatogram of sample No. 4 of diesel blow-by gas.

Table 2. VOLATILE ORGANIC VAPORS IDENTIFIED IN DIESEL BLOW-BY GAS (SAMPLE NO. 6)

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
1	80	CO_2
2	81	*n*-hexane
2A	82	C_7H_{16} isomer
2B	82	C_7H_{14} isomer
3	83	*n*-octane
3A	84	C_9H_{20} isomer
4	85	*n*-nonane
4A	85	$C_{10}H_{22}$ isomer
5	87	*n*-decane
5A	88	$C_{11}H_{24}$ isomer
5B	88	$C_{10}H_{20}$ isomer
6	91	*n*-undecane
6A	92	$C_{11}H_{22}$ + $C_{12}H_{26}$ isomers
7	94	$C_{12}H_{26}$ isomer
8	96	toluene
8A	97	$C_{12}H_{24}$ isomer
8B	97	$C_{14}H_{30}$ isomer
9	101	*n*-tridecane
9A	102	ethylbenzene + $C_{13}H_{26}$ isomer
9B	103	*p*-xylene
9C	104	$C_{14}H_{28}$ isomer
10	105	2-hexanol
11	107	*o*-xylene
11A	108	C_3-alkyl benzene isomer
11B	108	$C_{13}H_{24}$ isomer
12	111	$C_{14}H_{30}$ isomer
13	114	*n*-tetradecane
13A	115	C_3-alkyl benzene isomer
13B	117	$C_{15}H_{30}$ isomer
14	118	$C_{16}H_{34}$ isomer
14A	119	C_4-alkyl benzene isomer
14B	121	$C_{15}H_{30}$ isomer
14C	123	alkyl alcohol isomer (?)
15	124	*n*-pentadecane
15A	125	C_4-alkyl benzene isomer
15B	126	$C_{15}H_{28}$ isomer
16	128	$C_{16}H_{32}$ isomer
16A	130	C_5-alkyl benzene isomer
17	133	$C_{16}H_{34}$ isomer
18	135	$C_{16}H_{34}$ isomer
19	140	$C_{16}H_{30}$ isomer
20	142	C_7H_{34} isomer
21	144	$C_{17}H_{36}$ isomer
22	146	$C_{18}H_{36}$ isomer
23	149	$C_{17}H_{34}$ isomer
24	151	$C_{19}H_{38}$ isomer
25	153	acetic acid (tent.) + $C_{18}H_{38}$ isomer
27	161	$C_{14}H_{20}$ isomer (tent.)
28	165	N,N-dimethylacetamide
29	174	phenyl acetate
31	180	aliphatic acid (?)
31A	180	acetophenone
32	184	naphthalene
33	184	N-methylacetamide
34	190	aliphatic acid (?)
35	192	$C_{15}H_{24}O$ isomer (tent.)
37	195	methylnaphthalene isomer
38	198	$C_6H_{10}O$ isomer (tent.)
39	200	methylnaphthalene isomer
40	203	diethylphthalate
40A	203	C_2-alkyl naphthalene isomer
41	205	dimethylnaphthalene isomer
42	205	dimethylnaphthalene isomer
43	205	dimethylnaphthalene isomer
44	205	phenol
45	205	dimethylphenol isomer
45A	205	C_3-alkyl naphthalene isomer
46	205	cresol isomer
47	205	cresol isomer
48	205	C_3-alkyl naphthalene isomer
51	205	dimethylphenol isomer
52	205	ethylphenol isomer
53	205	C_2-alkyl phenol isomer

precursors for the formation of N-nitrosoamines were present such as dimethylamine, diethylamine, dipropylamine, etc. and/or morpholine. There was no evidence of the presence of amines in this sample, however two nitrogen containing compounds, N,N-dimethylacetamide and N-methylacetamide were observed.

4.0 References

1. Research in RTI Laboratories under EPA Contract No. 68-02-1228, Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors, 1976 (in preparation).
2. Cohen, J., EPA-NFIC, Denver, CO, private communication.
3. Pellizzari, E. D. Development of Method for Carcinogenic Vapor Analysis in Ambient Atmospheres. Publication No. EPA-650/2-74-121, Contract No. 68-02-1228, 148 pp., July, 1974.
4. Pellizzari, E. D. Development of Analytical Techniques for Measuring Ambient Atmospheric Carcinogenic Vapors. Publication No. EPA-600/2-75-076, Contract No. 68-02-1228, 187 pp., November, 1975.
5. Pellizzari, E., J. E. Bunch, R. E. Berkley and J. T. Bursey, Biomed. Mass Spec., 3, 196 (1976).
6. Pellizzari, E. D., J. E. Bunch, J. T. Bursey, R. E. Berkley, E. Sawicki and K. Krost, Anal. Lett., 9, 579 (1976).

Table 3. VOLATILE ORGANICS IN DIESEL BLOW-BY GAS[a]

SAMPLE 5

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
1	40	CO_2
2	43	1-butene
3	47	acetaldehyde
3A	47	isopentane
4A	48	C_5H_{10} isomer
5	49	2-pentane
5A	50	$C_4H_{10}O$ isomer
6	50	acetone
7B	53	CS_2 (tent.)
8	56	2-methylpentane
8A	57	C_4H_3O isomer
9	57	3-methylpentane
9A	58	C_6H_{12} isomer
10	59	hexafluorobenzene (e[illegible])
10A	60	n-hexane
12	64	methylcyclopentane + perfluortoluene (e[illegible])
12A	66	methyl ethyl ketone (tent)
12C	68	C_7H_{14} isomer
13	69	benzene
13B	70	cyclohexane
13C	71	2-methylhexane
14	73	3-methylhexane
14A	74	C_7H_{14} isomer
15	75	C_8H_{18} isomer
15A	76	+ C_7H_{12} isomer
16	77	n-heptane
16A	78	C_7H_{14} isomer
16B	79	n-pentanal
16C	79	C_7H_{12} isomer
16D	81	2-pentanone
17	82	methylcyclohexane
18	84	C_8H_{18} isomer
18A	85	C_8H_{16} isomer
19	88	4-methyl-2-pentanone
20	89	toluene
20A	90	4-methyl-2-pentanone
21	92	C_8H_{18} isomer
22	93	C_8H_{16} isomer
22A	94	C_8H_{14} isomer (tent)
23	95	C_8H_{16}
23A	97	C_8H_{14} isomer
25	98	tetrachloroethylene
25A	100	$C_6H_{12}O$ isomer
26	101	C_7H_{14} isomer (tent)
27	103	C_9H_{20} isomer
28	104	methyl ethylcyclopentane isomer
28A	106	C_9H_{18} isomer
29	107	C_9H_{18} isomer
30	108	ethylbenzene isomer
30A	109	C_9H_{20} isomer
31	110	p-xylene
31A	110	C_9H_{20} isomer
32	112	C_9H_{20} isomer
33	113	diacetone alcohol (tent.)
33A	113	styrene
33B	114	o-xylene
33C	114	C_9H_{18} isomer
34	115	N,N-dimethylacetamide
35	117	2-nonane
37	120	isopropylbenzene
38	122	$C_{10}H_{22}$ isomer
39	123	C_3-alkyl cyclohexane isomer
40	124	$C_{10}H_{22}$ isomer
41	125	$C_{10}H_{22}$ isomer
41A	125	n-propylbenzene
42	126	unknown
43	127	ethyltoluene isomer
44	129	trimethylbenzene + $C_{10}H_{22}$ isomers
45	130	$C_{10}H_{22}$ isomer
45A	131	$C_{10}H_{20}$ isomer
45B	132	$C_{10}H_{20}$ isomer
46	133	1,2,4-trimethylbenzene + $C_{10}H_{20}$ isomer
47	136	phenol + n-decane
47A	137	C_4-alkyl benzene isomer
47B	138	C_4-alkyl benzene isomer
48	139	1,2,3-trimethylbenzene + $C_{11}H_{22}$ isomer
49	141	$C_{11}H_{24}$ isomer
50	142	indan (tent) + $C_{11}H_{20}$ isomer
51	143	C_4-alkyl cyclohexane isomer
52	144	$C_{11}H_{22}$ isomer
53	145	C_4-alkyl benzene + $C_{10}H_{16}$ isomer

TABLE 3 (Cont'd). VOLATILE ORGANICS IN DIESEL BLOW-BY GAS[a]
SAMPLE 5

Chromatographic Peak No.	Elution Temp. (°C)	Compound
54	145	C_4-alkyl benzene + $C_{11}H_{22}$ isomers
55	146	$C_{11}H_{24}$ isomer
56	147	$C_{10}H_{18}$ isomer
57	148	$C_{11}H_{24}$ isomer
58	149	C_4-alkyl benzene isomer
58A	150	$C_{11}H_{22}$ isomer
59	150	C_4-alkyl benzene + $C_{12}H_{22}$ isomers
59A	151	$C_{11}H_{22}$ isomer
60	152	$C_{11}H_{22}$ isomer
60A	153	C_3-alkyl benzene + cresol isomers
61	154	n-undecane
62	156	$C_{11}H_{22}$ isomer
62A	156	C_4-alkyl benzene isomer
62B	157	$C_{12}H_{26}$ isomer
63	157	$C_{11}H_{20}$ + $C_{14}H_{20}$ isomers (tent.)
63A	158	$C_{12}H_{20}$ isomer
64	159	$C_{12}H_{26}$ isomer
64A	159	C_5-alkyl benzene isomer
64B	160	$C_{11}H_{20}$ isomer
65	160	C_5-alkyl cyclohexane isomer
65A	161	$C_{12}H_{24}$ isomer
66	162	C_4-alkyl benzene isomer
67	163	$C_{12}H_{26}$ isomer
67A	163	C_2-alkyl phenol isomer
68	164	C_4-alkyl benzene isomer
69	165	$C_{12}H_{26}$ isomer
70	166	C_2-alkyl phenol isomer
71	167	$C_{12}H_{22}$ isomer
71A	168	naphthalene
72	169	$C_{12}H_{24}$ isomer
73	171	n-dodecane
74	173	$C_{13}H_{28}$ isomer
74A	173	$C_{13}H_{26}$ isomer
75	174	C_6-alkyl benzene isomer
76	175	C_7-alkyl benzene + $C_{13}H_{26}$ isomers
77	176	$C_{12}H_{22}$ isomer
77A	176	$C_{13}H_{26}$ isomer
78	177	C_6-alkyl cyclohexane isomer
79	178	$C_{13}H_{28}$ isomer
80	179	$C_{13}H_{26}$ isomer
81	180	$C_{13}H_{28}$ isomer
82A	182	$C_{13}H_{24}$ isomer
82B	183	$C_{13}H_{26}$ isomer
83	184	$C_{14}H_{28}$ isomer
84	185	β-methylnaphthalene + n-tridecane
85	187	$C_{12}H_{22}$ isomer
86	188	α-methylnaphthalene
86A	188	$C_{14}H_{30}$ isomer
86B	190	$C_{14}H_{26}$ isomer
87	191	$C_{14}H_{28}$ isomer
88	192	C_7-alkyl cyclohexane isomer
89	194	$C_{14}H_{26}$ isomer
90	194	$C_{14}H_{30}$ isomer
91	196	$C_{15}H_{30}$ isomer
92	197	$C_{15}H_{32}$ isomer
92A	199	$C_{15}H_{28}$ isomer
93	200	n-tetradecane
94	201	C_2-alkyl naphthalene isomer
94A	202	$C_{15}H_{30}$ isomer
95	203	C_2-alkyl naphthalene isomer
96	204	$C_{15}H_{30}$ isomer
96A	204	$C_{15}H_{28}$ isomer
96B	206	$C_{15}H_{28}$ isomer
97	206	C_8-alkyl cyclohexane isomer
98	208	$C_{16}H_{34}$ isomer
99	210	$C_{15}H_{28}$ isomer
100	211	$C_{16}H_{32}$ isomer
101	213	n-pentadecane
101A	214	C_3-alkyl naphthalene
101B	215	$C_{15}H_{30}$ isomer
102	217	C_3-alkyl naphthalene + $C_{16}H_{32}$ isomers
103	219	$C_{16}H_{30}$ + $C_{17}H_{34}$ isomers
104	220	C_9-alkyl cyclohexane isomer
105	221	$C_{16}H_{30}$ isomer
106	222	alkyl phthalate isomer (BKG)
107	224	2,2,4-trimethyl penta-1,3-diol di-isobutyrate (BKG)
108	225	n-hexadecane
109	230	$C_{17}H_{34}$ isomer
110	232	$C_{18}H_{38}$ isomer
111	233	C_{10}-alkyl cyclohexane isomer
112	234	$C_{17}H_{34}$ + $C_{17}H_{32}$ isomers
113	236	$C_{18}H_{36}$ isomer
114	238	n-heptadecane
115	239	$C_{17}H_{34}$ isomer (tent.)

TABLE 3 (Cont'd). VOLATILE ORGANICS IN DIESEL BLOW-BY GAS[a]
SAMPLE 5

Chromato-graphic Peak No.	Elution Temp. (°C)	Compound	Chromato-graphic Peak No.	Elution Temp. (°C)	Compound
116	240	$C_{18}H_{36}$ isomer			
116A	240	$C_{19}H_{38}$ isomer			
117	240	C_{11}-alkyl cyclohexane isomer			
118	240	n-octadecane			
119	240	$C_{19}H_{40}$ isomer			

[a] Analysis was performed on a 100 m glass SCOT column coated with OV-101 programmed from 20-240°C @ 4°/min. Carrier flow (He) was 2.25 ml/min.

APPENDIX D

CATERPILLAR TRACTOR COMPANY REPORT TO EPA ON DIESEL CRANKCASE EMISSIONS

CATERPILLAR TRACTOR CO.

TECHNICAL CENTER

Peoria, Illinois 61629

February 10, 1976

Mr. C. T. Hare, Manager
Advanced Tech.
Department of Emissions Research
Southwest Research Institute
8500 Culebra Road
San Antonio, TX 78228

Dear Mr. Hare:

During my February 4 visit to Southwest Research Institute you indicated that EPA remains curious about crankcase blowby gas from diesel engines as an atmospheric pollutant. Enclosed is a copy of my June 19, 1974, letter to John McFadden and a copy of a Caterpillar report dated June 6, 1974.

I hope this report will contribute to your investigation. We have done no further checking since this report was written since we are convinced that diesel blowby is an insignificant air pollution source. If you have questions, let me know.

Very truly yours,

Don Henderson

Emissions Control Manager
Engineering G.O.

R. D. Henderson
Telephone: (309) 578-6112
jcc

Encs.

REPORT BY

CATERPILLAR TRACTOR CO.

to

U. S. ENVIRONMENTAL PROTECTION AGENCY

OFFICE OF AIR PROGRAMS

TO SUPPLY

INFORMATION ON DIESEL ENGINE

CRANKCASE BLOWBY ANALYSIS

AND

DISPOSAL SYSTEMS

JUNE 6, 1974

Introduction

The purpose of this report is to provide the U. S. Environmental Protection Agency with diesel engine crankcase blowby information. This is necessary because diesel blowby gas may be mistakenly considered an air pollution source of sufficient magnitude to justify future regulatory control. Currently the blowby gas from most diesels is discharged to the atmosphere.

Our measurements show that diesel engine crankcase blowby gas contributes very little to total engine emissions so control is not justified from that standpoint. Blowby gas disposal systems are used in some instances by Caterpillar Tractor Co. for commercial reasons but are not readily adapted to all engines, particularly those that are turbocharged.

Discussion

In the gasoline engine, crankcase blowby gas is a significant source of pollution, particularly hydrocarbons, while in the diesel it is not. This is primarily because of the fundamental difference in the method of mixing air and fuel. In spark ignition engines the mixing takes place in the carburetor resulting in a nearly homogenous fuel-air mixture flowing into the cylinders during the intake stroke. Thus, all cavities in the cylinder, including the volume above the top ring between the piston and the cylinder wall, are filled with the fuel mixture which isn't completely burned during the power stroke. Some of this unburned fuel escapes into the crankcase and is contained in the blowby gas.

In the diesel engine, fuel is not injected into the cylinder until late in the compression stroke so cylinder cavities such as the one around the piston above the top ring contain air only. The diesel also operates with excess combustion air so the fuel tends to be more completely consumed. Thus, the diesel engine tends to have lower amounts of HC in the exhaust and insignificant HC in the crankcase blowby gas.

For better understanding of this diesel characteristic, the blowby gas from a precombustion chamber, turbocharged V8 engine was analyzed and compared with the exhaust emissions using the EPA 13 mode diesel engine test as a basis. The following table shows the results:

	Exhaust - g/hp hr	Crankcase Blowby - g/hp hr	Blowby/Exhaust (Ratio)
CO	2.74	.0063	1/435
HC	0.41	.0125	1/33
NO_2	4.75	.0036	1/1320

In this engine the mass flow of the exhaust was approximately 200 times that of crankcase blowby. In order for the blowby to add significantly to total diesel engine emissions, the concentrations of CO, HC, and NO_x would have to be extremely high. We have concluded that the control of blowby gas is unnecessary from an emissions standpoint.

However, there are instances where diesel blowby gas is controlled in ways other than discharging directly to the atmosphere. The reasons are primarily commercial. Caterpillar Tractor Co. produces a medium duty naturally aspirated, V8 truck engine which has had a PCV system since its introduction. This was done at the request of a major customer.

In future low emission models of this engine we may not be able to use the PCV system which directs the blowby gas into the inlet manifold. This is because the blowby may cause soot particles from recriculated exhaust gas to deposit in the inlet manifold and ports to an unacceptable degree.

In a 500 hour test with EGR, excessive build up of deposits was experienced in the inlet manifold and inlet ports as shown in the attached photographs. As a result of this experience, EPA and Bureau of Mines (Bartlesville) people decided to discharge the blowby gases to the atmosphere when testing the durability of a Caterpillar 1160 model engine modified to reduce emissions. EGR was one of the emission control methods utilized. The test setup and results are reported in EPA-460/3-73-010, "Durability of Advanced Emission Controls for Heavy Duty Diesel and Gasoline Fueled Engines" by Fleming and French.

Return of crankcase blowby gas to the inlet manifold of a turbocharged engine presents significantly greater problems and may be completely impractical. Routing the gas through the turbo compressor wheel is not a good practice because dust may be caused to collect and reduce the compressor efficiency with resulting deterioration of engine performance. In the most extreme case, balance of the very high speed compressor wheel may be affected.

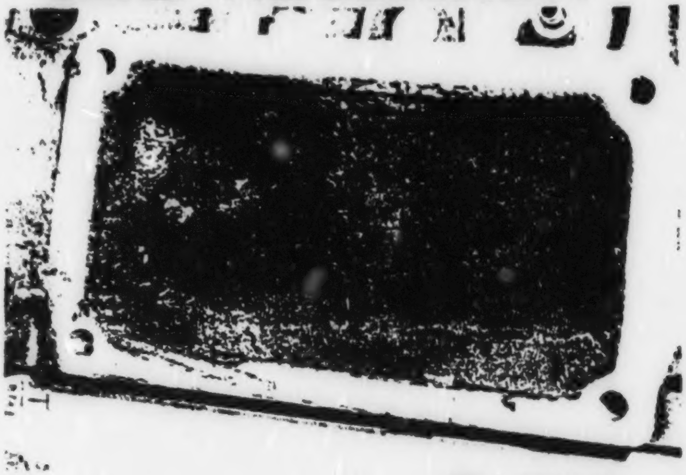
If blowby gas is introduced into the intake manifold after the compressor, a pump is necessary because of the higher pressure in the manifold. Even if a pump is used, there is still some likelihood of fouling the surfaces of the aftercooler core when one is used. Caterpillar currently does not consider return of blowby gases to the intake manifold in turbocharged engines a satisfactory or practical control method.

Although crankcase blowby gas is discharged to the atmosphere in most Caterpillar engines, this is done only after careful attention to breather design. Oil mist in the breather discharge is avoided by careful location of the outlet from the engine, by an effective system of baffles, and by maintaining suitably low gas velocity. The essentially oil free gas contains insignificant amounts of pollutants which escape from the combustion chamber into the crankcase as shown earlier in this report.

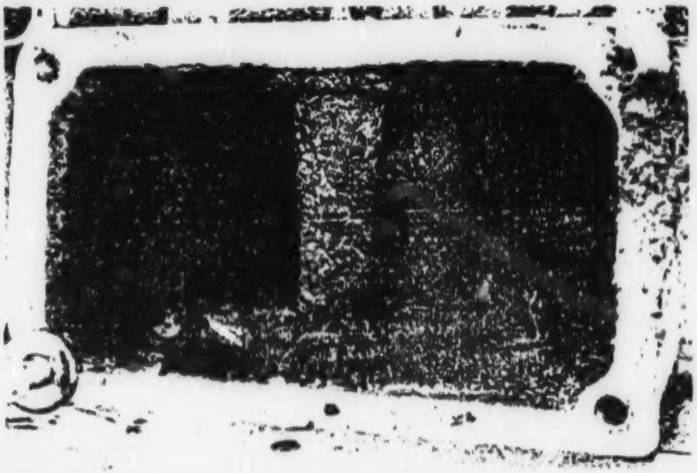
Conclusion

Preventing discharge of diesel crankcase blowby gas to the atmosphere is not justified from an emission control standpoint. When a PCV control system returning the gas to the intake manifold is used for commercial reasons, it should not be considered an emission control device.

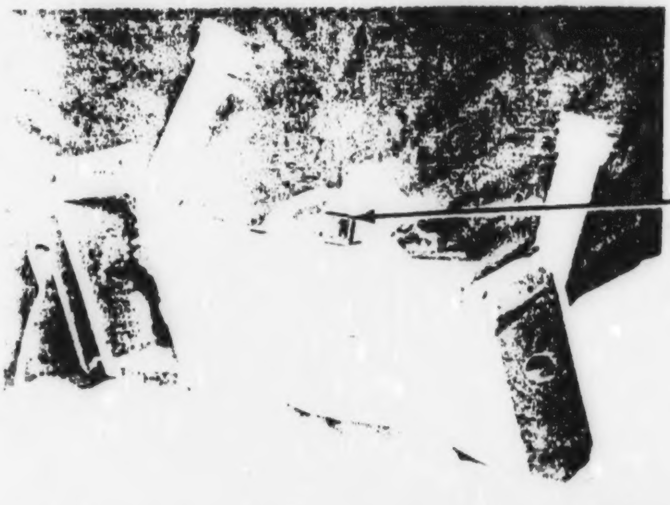
ENGINEERING
& RESEARCH



LEFT BANK CYLINDER
HEAD PLENUM CHAMBER
DEPOSITS AFTER 500
CYCLE ENDURANCE HRS



RIGHT BANK CYLINDER
HEAD PLENUM CHAMBER
DEPOSITS AFTER 500
CYCLE ENDURANCE HRS



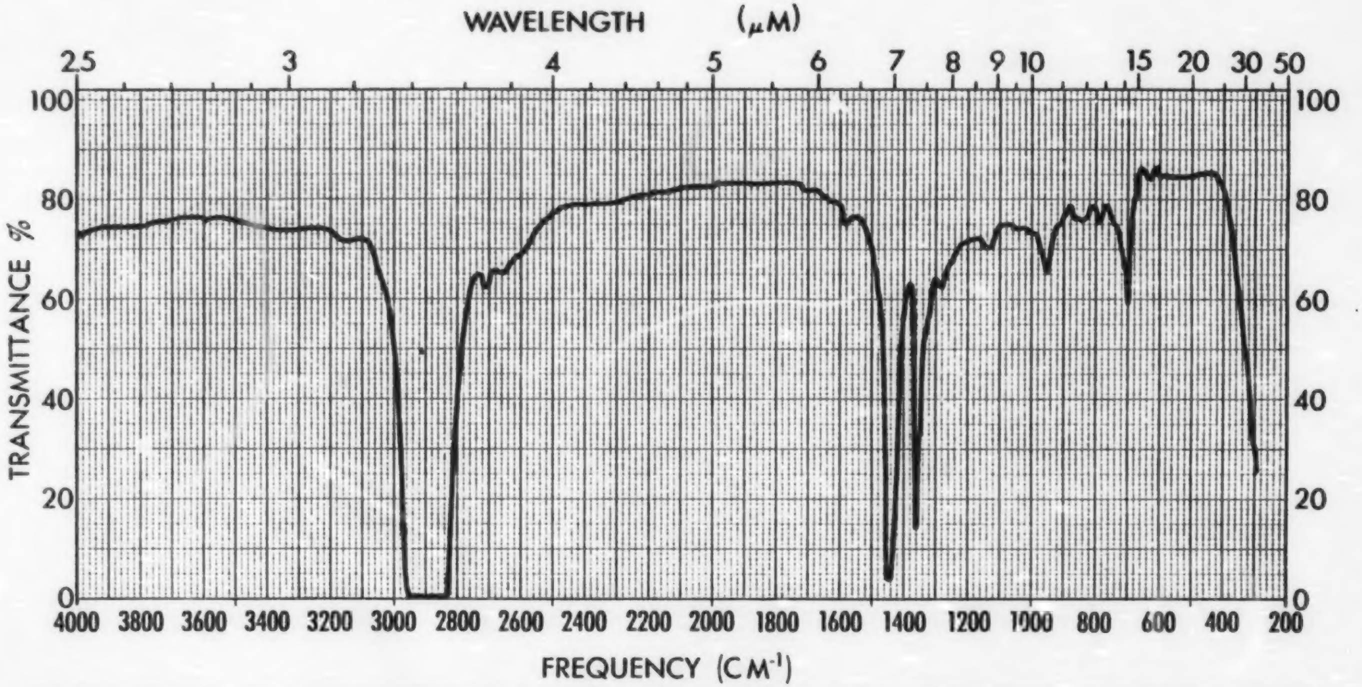
VIEW OF CROSSOVER (INTAKE) PIPE
FROM BOTTOM - 500 HOURS

BLOWBY UNDUCED HERE

NOTE: BLOWBY FLOWED MOSTLY TO LEFT BANK OF CYLINDERS. EGR INLET PORT IS PARTIALLY BLOCKED CAUSING UNEVEN BANK TO BANK RECIRCULATION

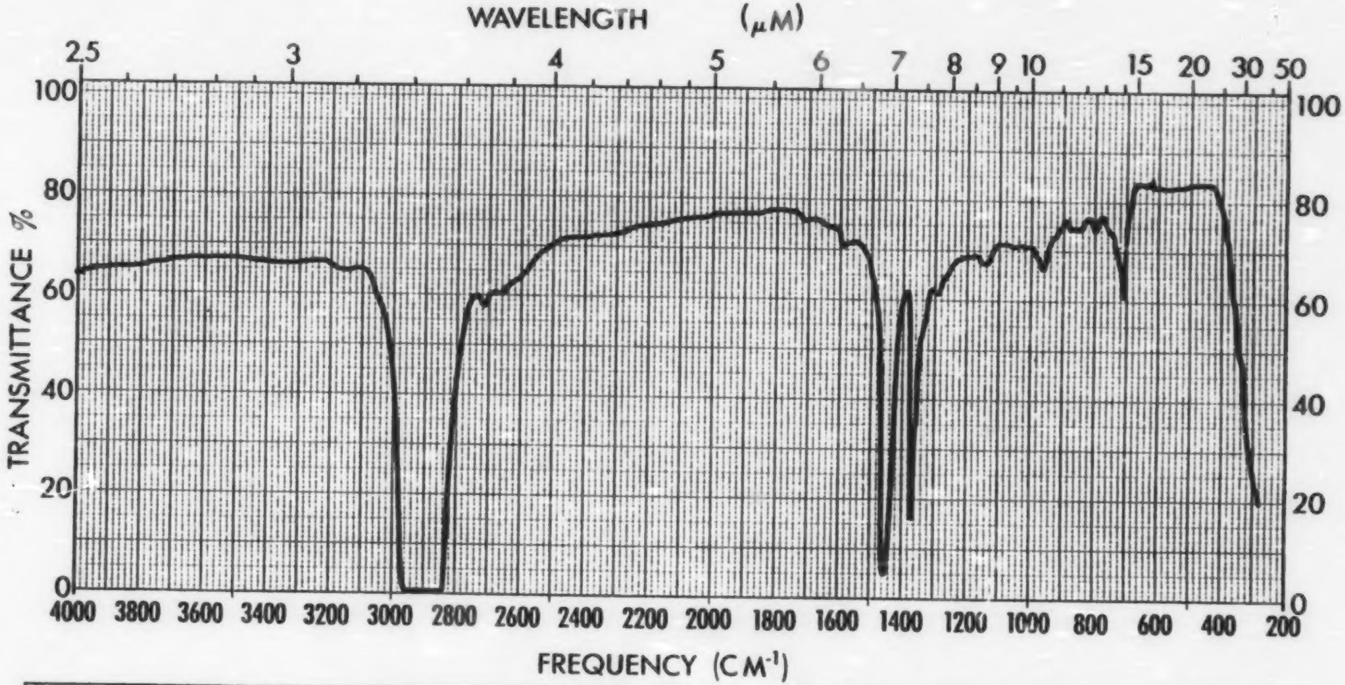
APPENDIX E

INFRARED SPECTRA OF LUBRICATING OILS



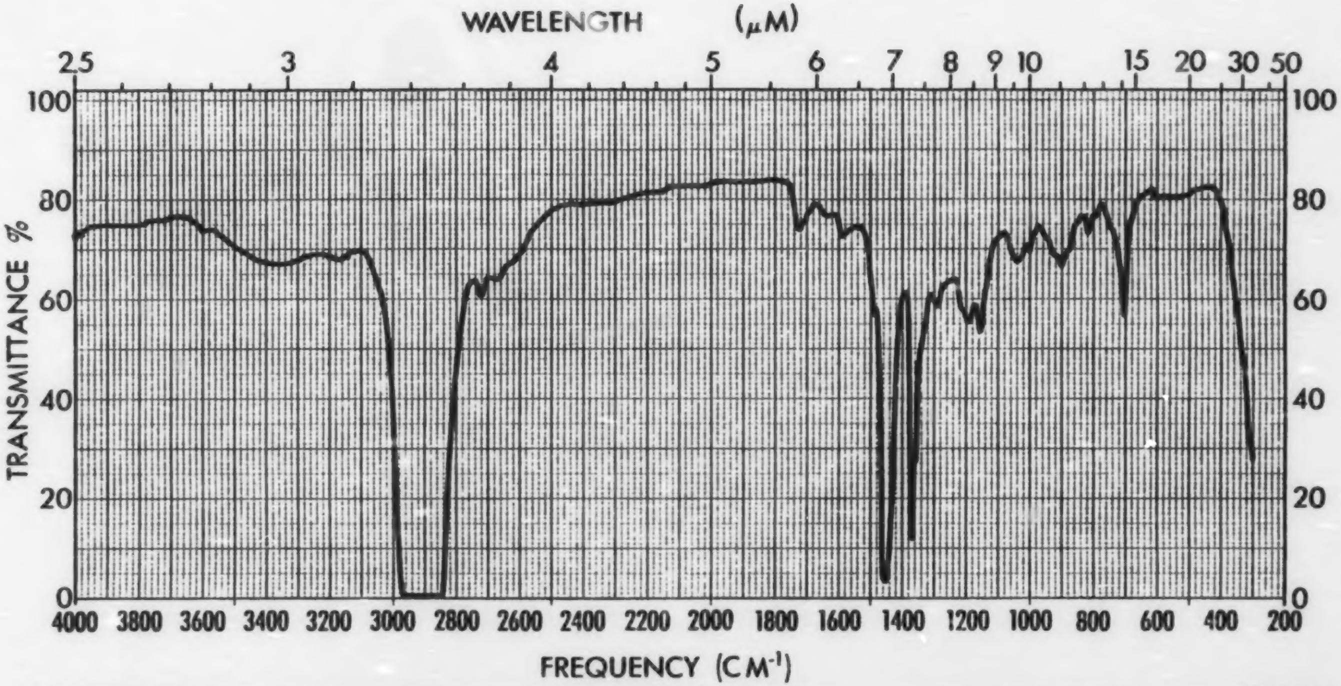
SPECTRUM NO. 900	ORIGIN	LEGEND	REMARKS
SAMPLE 6U-71		1.	
NEW OIL	PURITY	2.	
	PHASE	DATE 8-3-76	
	THICKNESS .025	OPERATOR D.B.	

SPECTRUM NO.
SAMPLE



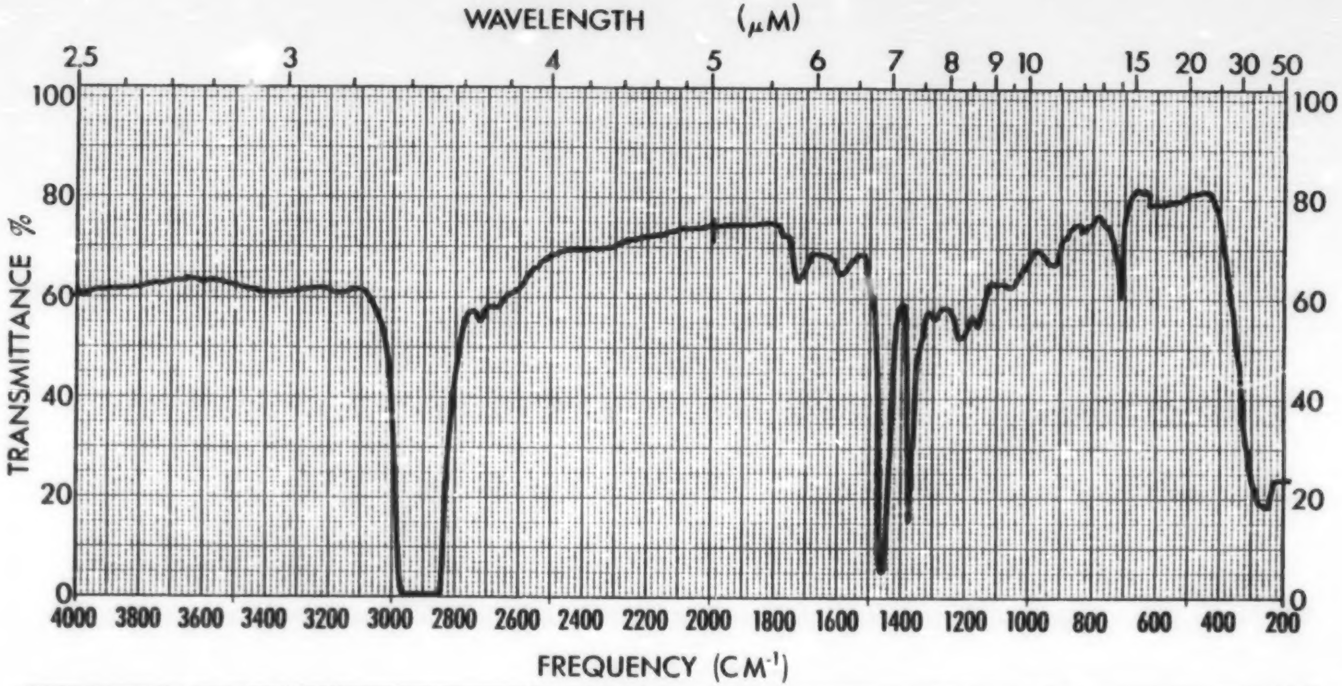
SPECTRUM NO. 901	ORIGIN	LEGEND	REMARKS
SAMPLE 6V-71		1.	
USED OIL	PURITY	2.	
	PHASE	DATE 8-3-76.	
	THICKNESS .025	OPERATOR D.B.	

SPECTRUM NO.
SAMPLE



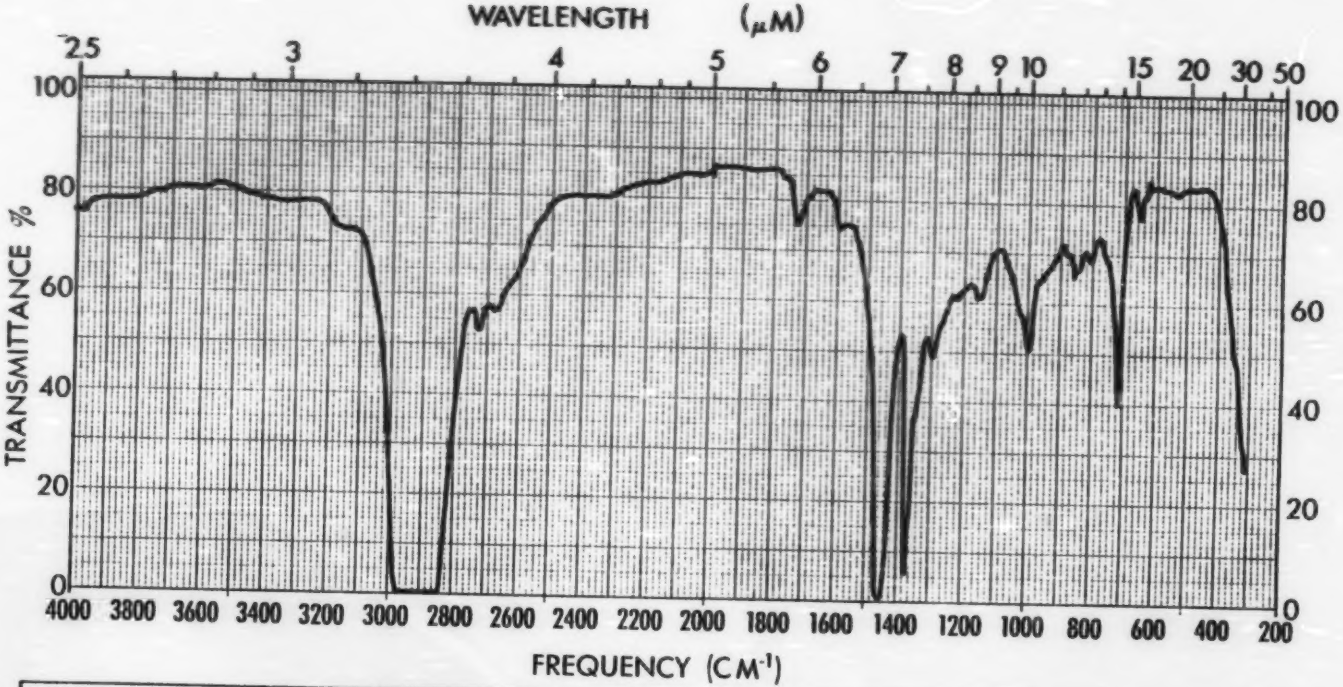
SPECTRUM NO. 902	ORIGIN	LEGEND	REMARKS
SAMPLE NTC-350		1.	
NEW OIL	PURITY	2.	
	PHASE	DATE 8-3-76	
	THICKNESS .025	OPERATOR D.B.	

SPECTRUM NO.
SAMPLE



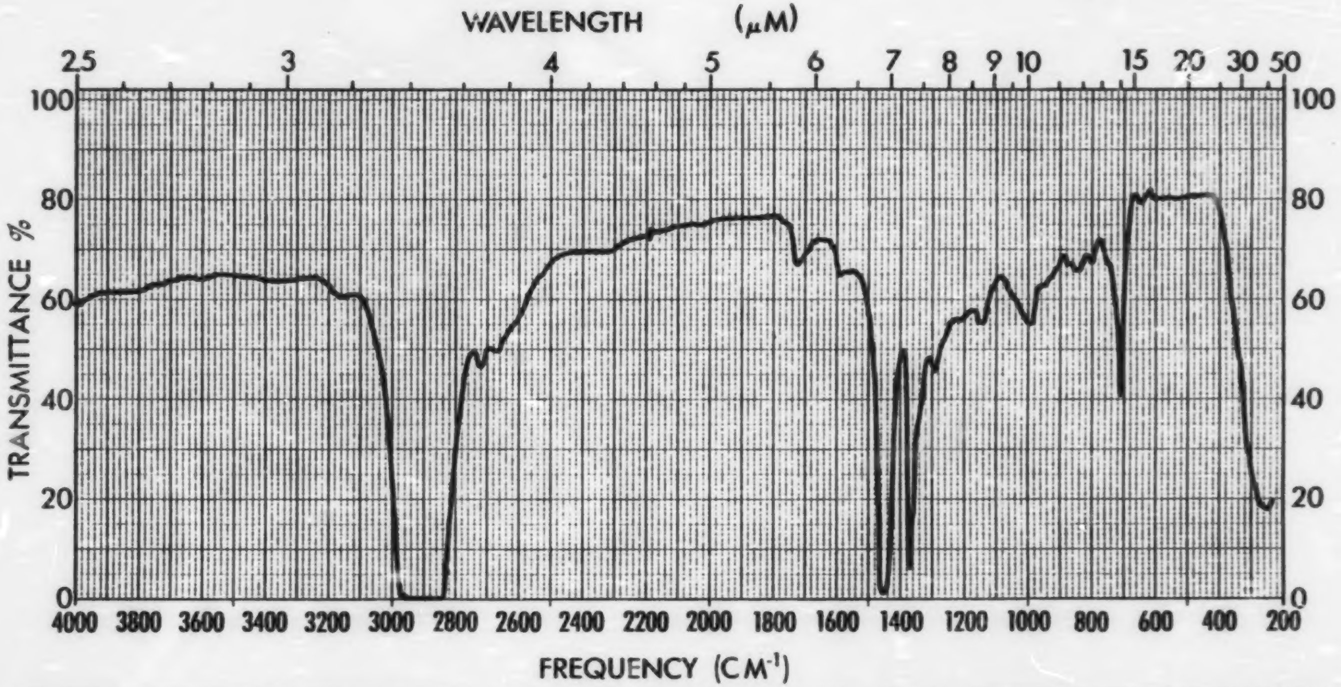
SPECTRUM NO. 903	ORIGIN	LEGEND	REMARKS
SAMPLE NTC-350		1.	
USED OIL	PURITY	2.	
	PHASE	DATE 8-3-76	
	THICKNESS 025	OPERATOR D.B	

SPECTRUM NO.
SAMPLE



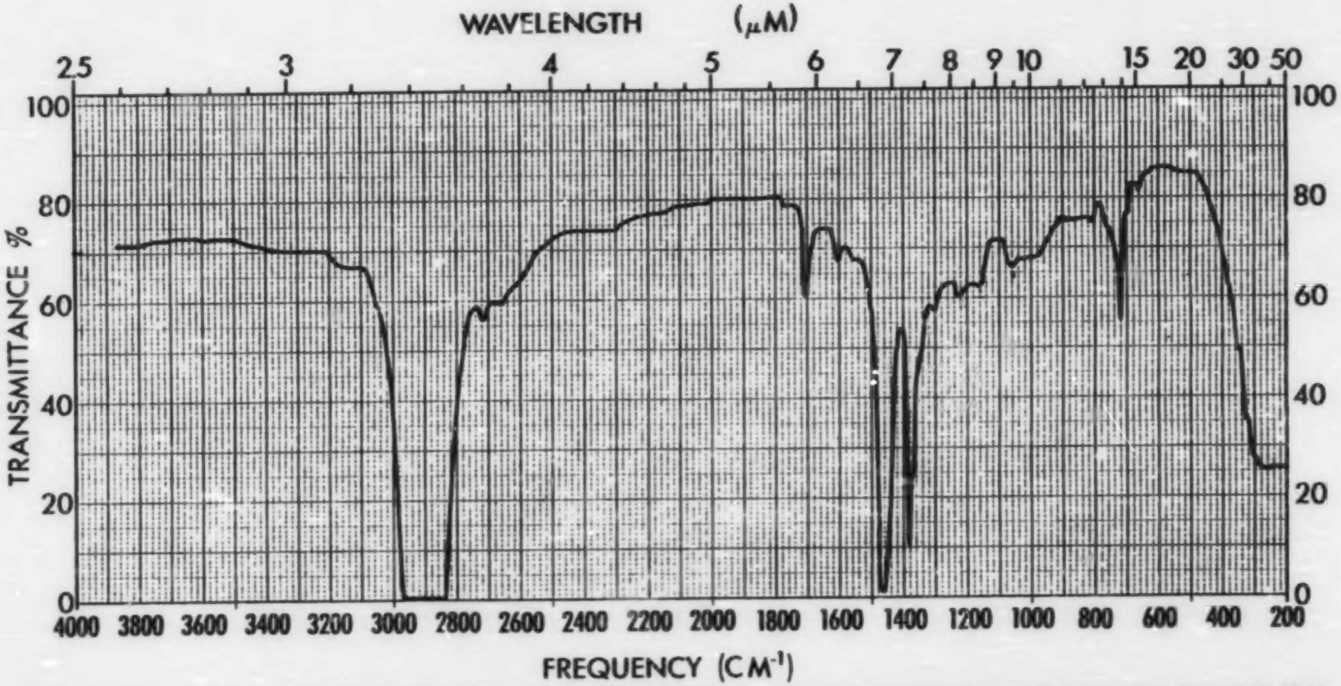
SPECTRUM NO. 930	ORIGIN	LEGEND	REMARKS
SAMPLE 6V-71		1.	
NEW OIL	PURITY	2.	
	PHASE	DATE 8-25-76	
	THICKNESS .05	OPERATOR D.B.	

SPECTRUM NO.
SAMPLE



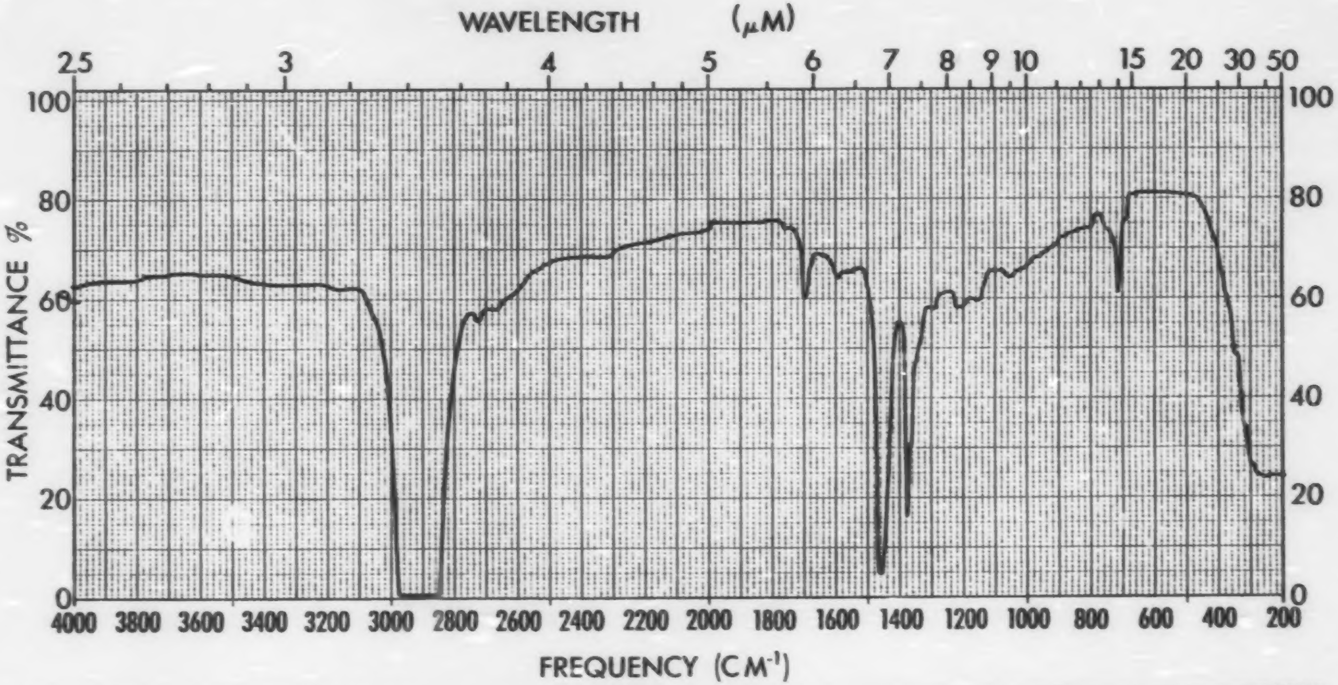
SPECTRUM NO. 931	ORIGIN	LEGEND	REMARKS
SAMPLE 6V-71		1.	
USED OIL	PURITY	2.	
	PHASE	DATE 8-25-76.	
	THICKNESS .05	OPERATOR D.B.	

SPECTRUM NO.
SAMPLE



SPECTRUM NO. 1166	ORIGIN	LEGEND	REMARKS
SAMPLE ETAY 1		1.	
	PURITY neat	2.	
	PHASE liquid	DATE 5/20/77	
	THICKNESS .025 mm	OPERATOR D	

SPECTRUM NO. 116
SAMPLE ETAY 1



SPECTRUM NO. 1167	ORIGIN	LEGEND	REMARKS
SAMPLE ETM 2		1.	
	PURITY neat	2.	
	PHASE Liquid	DATE 5/20/71	
	THICKNESS .025mm	OPERATOR B²	

SPECTRUM NO. 1167
SAMPLE ETM 2